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LITERATURE REVIEW FOR DEVELOPMENT OF THE MASTER ANALYTICAL SCHEME FOR ORGANIC COMPOUNDS IN WATER

by

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure specific contaminants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact and control of environmental contaminants, the Analytical Chemistry Branch characterizes chemical constituents of water and soil.

Chemists working in governmental, industrial, and academic laboratories have long recognized a need for a comprehensive analytical methodology for organic compounds in water. To this end, research was begun in 1978 to develop a qualitative-quantitative scheme for the analysis of organics of all volatility classes (amenable to gas chromatography), of almost all functional groups, in almost any water sample. The result is the Master Analytical Scheme for Organic Compounds in Water, a compilation of protocols that employ new techniques and modifications of existing analysis procedures. Users may apply the Scheme as a set of protocols for a comprehensive analysis or use individual protocols separately for analysis of organic fractions of particular interest. Among its many applications are epidemiological studies, wasteload allocations, permit application evaluations, trends analyses, watershed management studies, exposure assessments, landfill hazard evaluations, and aqueous source characterizations.

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PREFACE

Few individuals can be considered an expert in all areas of organic/analytical chemistry. Thus, while keeping in focus the primary aim of preparing a state-of-the-art review as a prelude for experimental development of a comprehensive analytical scheme, this review, current through June 1982, was also tailored to enlighten the novice. Subsequently, such a review might serve as a training manual for users of the scheme, now available from the National Technical Information Service as "Master Analytical Scheme for Organic Compounds in Water: Part 1, Protocols, and Part 2, Appendices."

ABSTRACT

A state-of-the-art review was prepared covering analysis of organics in drinking water and surface waters, and in waters from industrial, municipal, and energy sources. The areas reviewed included: (1) sampling; (2) techniques for component isolation and/or concentration; (3) extract fractionation; (4) chemical derivatization; (5) gas chromatography; (6) gas chromatography/mass spectrometry/computer techniques; and (7) quality control/quality assurance. The initial review was considered a prerequisite for experimental development of the EPA's Master Analytical Scheme for organics in water; it has been updated to include the appropriate literature through June 1982.

This report was submitted in partial fulfillment of Contract No. 68-03-2704 by Research Triangle Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1978 to July 1983, and work was completed as of July 1983.

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SECTION 1

INTRODUCTION

The overall thrust of this research program was to develop and/or validate methodologies for incorporation into a Master Analytical Scheme for the qualitative and quantitative analysis of volatile organic compounds in water using a gas chromatography/mass spectrometry/data system (GC/MS/DS) as the basic analytical tool.

The primary purpose of this state-of-the-art literature review was to provide a foundation for developent of a matrix of analytical operations (techniques) in order of their expected applicability to the Master Analytical Scheme. It is intended to be both a comprehensive and critical review of research results applicable to the analysis of organics in water. Equally important was the identification of deficiencies and voids in current methods and instrumentation. More specifically, we have discussed in this report analytical principles, amenability of compound types and water matrices to the various analytical techniques, and the inherent advantages and disadvantages of each technique.

A statement of the Master Analytical Scheme objectives and approaches should help the reader to better understand the objectives of this literature review, and thus its coverage. The MAS is intended to direct the user in the preferred way to perform the analysis of organics in water. It describes the approach to sampling any industrial or municipal effluent, surface water, or drinking water in such a manner as to obtain a sufficient volume of artifact-free sample for qualitative and quantitative analysis of any volatile organic compound. For the purpose of this program, volatile organics are defined as those which will either elute from a GC column at 300°C in one hour or less or which may be derivatized to meet this criterion. Volatile organics include: (1) highly volatile, purgeable compounds; (2) polar or ionic water soluble, nonpurgeable compounds; and (3) intermediate to low volatility, nonpurgeable but extractable compounds. Lower detection (LD) limits are dependent upon compound classes and type of water being analyzed; in general, LD's of 0.1 μg/L (drinking), 1 μg/L (surface), and 10 μg/L (effluents) are the goal of the scheme.

The user is guided as how to sample (batch or continuous), how and when to add internal standards, and how to handle and preserve the sample. Directions for extraction, concentration, and cleanup are given to allow maximum separation and recovery of the compound or class of compounds of interest to the user, or to allow a survey analysis of all organics to which the entire scheme applies. Furthermore, the user is then directed to use specified gas chromatographic parameters for separation and detection of all compounds of interest. Detected compounds are then identified by previously established GC/MS/DS techniques. The user of the Master Analytical Scheme will be able to quantify identified compounds using a computer program, MASQUANT, that calculates concentrations based on access to a data bank of MS response factors and recovery values for about 260 model analytes.

The user of the Master Analytical Scheme will not be bound to the use of all protocols, but can select those appropriate for the analysis of a single selected compound or one class of compounds that is of primary interest to him. The intention is to provide a flexible scheme which the user can apply to a comprehensive survey or adapt to rapid screening for specific organics with less quantitative accuracy than expected for detailed application.

In order to acquire the appropriate information to achieve the cited goals of a state-of-the-art review, information was retrieved from government reports and the open scientific literature. Furthermore, many investigators, listed in Appendix A, were contacted directly to obtain pertinent unpublished information. This updated version of the review includes the appropriate literature through June 1982.

SECTION 2

CONCLUSIONS

These conclusions constitute a summary of the analytical operations described and referenced in detail in Sections 3-9, and are arranged under the same major headings.

SAMPLING, PHASE SEPARATIONS, PRESERVATION, AND INTERNAL STANDARDS

Several issues must be addressed when sampling water from various sources. These are: (1) the sampling mode e.g., discontinuous or continuous sampling, (2) sample contamination, (3) vessel type, (4) phase separation, (5) addition of internal standards, and (6) preservation of the sample.

Environmental waters are generally not homogeneous systems, and aqueous organic contaminants do not exhibit true solution characteristics. In order to develop a comprehensive nonbiased scheme to adequately sample and analyze water matrices, it is necessary to know the identity of competing phases, their nature, their effect on organic and aquatic systems, and their behavior during workup and analysis. The general treatment of the three nonaqueous phases--particulates, colloids, and oils--has not been adequately studied by investigators. The general handling of these phase types will require investigation in order to define an approach which is compatible to the characterization of organics in true solution.

Particulates have been removed using filtration and centrifugation. Quantitative variation occurs between analyses for purgeable organics in samples with and without removal of particulates. Most investigators analyze purgeable organics in heterogeneous systems although the particulates may be removed when the nonpurgeables are examined. The handling of heterogeneous aqueous samples needs to be addressed.

In order to assess the degradation of a sample or the loss of compounds of interest, internal standard(s) should be added to the sample. This step is generally conducted in the laboratory; however, this might best be accomplished in the field at the time of collection. Review of the techniques utilized by investigators indicate a considerable diversity in approaches to quantification utilizing internal standards. Thus, this is an important area which needs better definition and possible standardization.

Samples are generally protected from photodecomposition by using amber glass bottles as sample containers and by incorporation of antimicrobial agents. Another process which can compromise the integrity of an aqueous sample is adsorption of the organic compounds onto the glass walls of the container. Addition of a nonpolar solvent has been used to minimize this problem. Quenching agents have been used to inhibit formation of organochlorine compounds in chlorinated samples such as drinking water or municipal wastewater. There is no unified technique for protecting the sample against decomposition or artifact formation.

In general, an assortment of methods have been utilized for the sampling, storage, and preservation of water samples. What is most needed is the validation of an approach for handling each type of water (drinking, surface, industrial, municipal, and energy) which accommodates the special problems potentially associated with these types of waters.

TECHNIQUES FOR SAMPLE COMPONENT ISOLATION AND/OR CONCENTRATION

Static Headspace Analysis

The static headspace analysis method is considered a simple, reproducible, and rapid technique for measuring volatile organic compounds in water; a method capable of high sample throughput. It is highly adaptable to water analysis and is used primarily for determining nonpolar compounds with boiling points less than 125°C. Due to their higher solubility, low molecular weight polar compounds are amenable to static headspace analysis only at high concentrations or at reduced pressure.

To more precisely define the scope of this technique, the percent recovery for a representative number of compounds (for the applicable chemical classes) needs to be determined. The static headspace method, however, may offer little advantage over the purge and trap or closed loop techniques.

Purge and Trap

The applicability of purge and trap to nearly any aqueous matrix identifies it as one of the more versatile techniques for determining highly volatile compounds in water.

Recovery studies have been conducted for a number of compounds but this has principally been restricted to those on EPA's priority pollutant list. It is a technique which exhibits high recoveries for compounds with boiling points less than 200°C and for compounds with moderate to low aqueous solubilities. The problem of high levels of particulates needs to be examined, since in some cases particulates have been found to limit compound recovery. Exhaustive recovery studies need to be conducted for a number of compounds in the applicable chemical classes for which information is still lacking.

Compounds which are highly water soluble can not be efficiently recovered using ambient temperature purge and trap, but increasing the water temperature during purging significantly improves recoveries. Recovery of compounds by purge and trap has also been found to depend on the sample matrix. Samples which contain appreciable quantitites of surface active materials tend to foam and, therefore, cannot be effectively purged. In cases where foaming cannot be controlled and is too severe to apply the purge and trap technique (through solution), then the alternate headspace purge technique may be employed.

For samples which are too complex to be resolved by high resolution gas chromatography, the development of schemes for preferentially trapping or separating classes of compounds would be desirable.

Closed-Loop Gas Stripping (Grob Technique)

This method may be one of the most promising techniques available for determining low levels of organic compounds in potable waters. Its advantages are the low detection limit and the broad molecular weight range of detectable compounds (up to C_{24}). Extraction efficiency is comparable with purge and trap for some nonpolar materials.

As with purge and trap, this technique exhibits no significant tendency for artifact formation for the compounds which have been examined. Since the purge gas essentially bathes the headspace of the sample, potential contamination from large quantities of purge gas is avoided.

One of the disadvantages of this technique is that it require specialized, structurally fragile, expensive, and not readily available equipment. The analysis time is long (3 hr strip time) thereby severely limiting sample throughput. The closed-loop gas stripping technique is not conducive to the simultaneous multiple analysis critical to routine water examinations and for the most part cannot be used with samples which tend to form. The efficiency and reproducibility of the entire method generally depends upon extraction of the charcoal filter, which is a delicate procedure and may vary considerably between users.

Research needs to be performed to determine the accuracy, reproducibility, and range of this technique.

Direct Aqueous Injection

The most significant advantages of direct aqueous injection lie in its intrinsic simplicity, low cost, and ease of automation. The absence of analytical preparative steps results in low systematic errors and relatively high precision. Coincident with this straightforward analytical scheme is a very low potential for sample contamination, resulting only from sampling and gas chromatographic injection techniques.

Some artifacts have been observed and have been contributed to the thermal decomposition of chlorinated nonpurgeable organic compounds (e.g., humic acids) leading to formation of lower molecular weight haloforms. Such artifacts seriously undermine the accuracy and applicability of the method for drinking water analysis, as most drinking waters contain both a chlorine residual from the disinfection process and some quantity of humic like materials. The effects of high salt content in aqueous samples has not been adequately investigated with this method, either.

The general technique has a limited sensitivity in the electron capture mode of 0.1 to 500 ppb, with approximately 50 ppb for aliphatic alcohols, acids and ketones using flame ionization detection. Amines have been detected by flame ionization at 10 ppb; 500 ppb is the limit for methanol.

Direct aqueous injection may sometimes be a satisfactory alternative to closed-loop stripping and purge and trap methods since this technique circumvents the inability to recover nonpurgeable highly water soluble compounds by the former techniques.

Steam Distillation

This procedure was primarily developed to collect aqueous distillates for concentrating polar, water soluble, low molecular weight compounds. It is applicable, for example, to the analysis of methanol, ethanol, acetone, 2-propanol, and methyl ethyl ketone, giving high and reproducible recoveries for these compounds. For the alcohols, the general limit of detection is 4-8 ppb.

Extractive distillation concentrates nonpolar, semivolatile compounds. Compounds successfully extracted include various pesticides, trichlorobenzenes, naphthalene, chlorophenol, nitrophenol, dimethylphenol, phenol, chloronaphthalene, fluorene, diethylphthalate, dinitrobenzene, anthracene, fluoroanthene, pyrene, and ethylhexyl phthalate. Emulsions and interferences commonly observed in solvent extraction are minimized or eliminated. It is concurrently an effective cleanup technique wherein inorganic salts and lipids are separated and left as a residue in the boiling flask.

The main problem with steam distillation is the time involved in the analysis. Depending on the sample type, volume, and contaminant levels, extraction may require a matter of hours or days, particularly in the case of clean water samples. The process is time-consuming and restrictive as to the number of and volume of samples that can be analyzed. The utilization of high temperature and prolonged heating has lead to artifact formation.

Reverse Osmosis

The major advantage of reverse osmosis is its ability to concentrate organics from a very large water sample. Reverse osmosis does not involve a phase change and, therfore, is not as discriminatory against hydrophilic polar organics. Reverse osmosis has been primarily used as a commerical technique for removing inorganic ions during water treatment rather than for trace level analysis of organic compounds. Commercially available systems, therefore, have large dead volumes in the feed compartment (8 gallons or greater) which means that very large samples must be processed in order to achieve adequate concentration.

Commercially available membranes are not designed specifically for organic rejection and, therefore, do not always have the desired characteristics. Contamination of the sample is a frequent problem with these membranes since they generally contain plasticizers.

This technique does exhibit some promise for organic analysis if membrane technology is improved to overcome some of the current problems.

Freeze-Drying/Lyophilization

Freeze-drying has been found to be suitable for water soluble, nonvolatile compounds or labile biological and other heat sensitive materials. Among the compounds concentrated using this technique have been fatty acids, carbohydrates, amino acids, nucleotides, urea, mannitol, xylitol, and organophosphates. In the process of concentration, most of the volatile organics are lost, particularly if they are not bound to any dissolved solids. Very little recovery data are available for environmental samples.

Lyophilization is applicable to all water types and biological materials. It is a preferred method for compounds that are heat sensitive and prone to artifact formation. However, it is a very time-consuming high energy process when large sample volumes are involved. Its low throughput and the loss of volatile compounds limit its applications.

Ion-Exchange

The major advantage of ion-exchange resins has been the ability to concentrate low molecular weight, ionic organics. It is an effective technique that provides both high concentration factors and good recoveries for amino acids, amines, and low molecular weight and polycarboxylic acids. Because most ion-exchange resins perform as accumulator columns, it is possible to process large volumes of water to provide very high concentration factors. It is a selective process which adsorbs only certain organics.

Many of the disadvantages of ion-exchange are those inherent to sorbent resin techniques. First, resins will adsorb only dissolved species; organics adsorbed on particular matter or associated with high molecular weight humic or fulvic acids will not be concentrated. Ion-exchange techniques are particularly sensitive to matrix effects. Second, resin accumulation often does not result from a single type of reaction. Although electrostatic attraction is the major driving force for accumulation, all resins contain a hydrocarbon backbone that can lead to hydrophobic adsorption. For example, low accumulations of neutral organics on ion-exchange resin during phenol analysis have been reported.

Concentration using ion-exchange resins has been report for drinking and surface waters and municipal, industrial, and energy effluents. Problems with each of these matrices have varied considerably depending upon the nature of concentration of interfering species. Waters with high levels of inorganic ions including sea water, some waste effluents and very hard or alkaline water will prematurely exhaust resin capacity or cause preferential exchange with sorbed organics.

Ion-exchange is a well established technique for removing or concentrating ionic species from water. Additional research needs to be performed to define the recoveries of various ionic chemical groups using ion-exchange techniques.

Sorbent Columns

Sorbent columns have been primarily used with clean water samples. They have not been well characterized for breakthrough and operating parameters, e.g., flow rate, column dimensions, etc. Accumulator columns have a tendency to be easily clogged and thus the presence of particulates must be studied in order to ascertain the maximum particulate load that is acceptable for a particular sorbent type, or a phase separation step must be included in the procedure. Contamination problems have been noted with activated carbon and XAD resins if they dry out. Sorbent columns could prove extremely versatile for the concentration of trace organics from large quantities of water and for preferentially adsorbing particular compound classes.

While the XAD resins look primising for use in sorbent columns, further developmental work is necessary if they are to be used routinely. One difficulty is the use of ether or dichloromethane as an eluting solvent since both of these solvents are immiscible with the water remaining on the surfaces of the sorbent particles. Recovery of the adsorbed compounds can be adversely afected by the inability of the eluting solvent to penetrate the water layer. Parameters of adsorption and desorption have not been completely delineated and often organic material cannot be removed from the resin. Resin columns degrade when dry and may give severe contamination if not maintained wet at all times. This may prove to be particularly troublesome if elution of organics is not performed immediately. Sorbent columns will not extract organics from particulates; thus, it is restricted to the removal of organics in solution. Further work needs to be directed to optimize the volume, flow rate, pH, and ionic strength of the sample for analysis for a particular compound or class of compounds. Other studies need to focus on stability of the adsorbed material on the resin, including longer term storage stability. This may open the possibility of on-site sampling and shipment of loaded columns to the laboratory for further storage and analysis.

Solvent Extraction

Liquid-liquid extraction (LLE) is considered a simple, rapid, and rather clean extraction procedure. It has been well studied in terms of recoveries and applicability of hydrophobic compounds. The limiting factor for all extraction methods is the distribution coefficient of the analyte between the water and the solvent. For polar substances, the distribution favors the water phase and these compounds are extracted with poor efficiency by LLE methods.

Water samples that contain high levels of surface active agents tend to form emulsions during mixing. A number of classical approaches have been taken to overcome these problems, namely: heating, salting out, centrifugation, settling, and mechanical disruption. The effect of these techniques is usually marginal.

Liquid-liquid extraction techniques will accumulate all hydrophobic compounds including high molecular weight organics (e.g., humic or fulvic acids, etc.). These materials may cause significant background interferences during gas chromatography, as well as limit final sample concentration.

Two serious limitations of the continuous LLE methods are that they are time-consuming and require expensive apparatus. Sample throughput is also low.

Solvent Evaporation

Frequently, the isolation of organic constituents from water involves significant quantitites of solvent that must be reduced or completely removed prior to analysis to effectively increase the overall sensitivity of the technique. Several methods have been reviewed including rotary evaporation, vacuum evaporation, free evaporation, and elevated temperature evaporation (Kuderna-Danish concentrator) with the latter being by far the most popular for environmental samples. Rotary evaporation can be used only for compounds of low volatility since the evaporation of solvent from the walls of flasks exposes solute to the evaporation process. As with rotary evaporation, vacuum evaporative techniques suffer from solute losses by volatilization so are also only applicable to solutes of low volatility.

The most successful application of the K-D apparatus occurs with quite volatile solvents and relatively nonvolatile solutes. As the volatility of the solute increases so does the potential for evaporative losses.

Free evaporation, where solvent is removed by passing a gas stream over the liquid surface, is predominately used for further evaporation of small solvent volumes and is applicable only to compounds of low vapor pressure.

The use of solvent evaporation techniques for quantititative analysis requires determination of the losses of volatile compounds for each of the chemical classes of interest. A study of compounds of various classes has already been conducted and should be confirmed.

FRACTIONATION

Noncolumn Techniques

Solvent partition processes depend on the preferential distribution of solutes into one of the two intermittently contacted but immiscible liquid phases. Solute solubility properties may be altered by controlling the pH of the aqueous phase, which is the basis for the familiar acid/base wash sequences used to an advantage in numerous extraction systems. Partition schemes have been employed in the analysis of ground water, surface waters, industrial waters, municipal waters, and drinking water. The selectivity of the solvent partition process has provided the greatest advantage in its use. Desired components have often been selectivity partitioned into a single fraction well separated from major interferences.

The usual problems attendant to the use of quantities of solvent (emulsion formation, greater sample manipulation, solvent removal) represent the major disadvantages. In addition, there is the possibility that analyte degradation may occur, particularly during acid or base treatment. The literature provides little information regarding this point.

Column Techniques

Column chromatography can be regarded in two forms: open column and high performance (HPLC), which differ primarily in the degree of resolution possible and the extent of instrument sophistication required. Practically all of the chromatographic modes (normal phase, reverse phase, ion-exchange, and gel permeation) have been used in environmental analysis. They serve as powerful tools and have been particularly useful when used in combination with other analytical operations for further separation of complex mixtures. Because of the extremely large number of permutations possible between the materials available for column chromatography and the solvent combinations used for effecting the chromatography it is virtually impossible to adequately treat this subject matter or address this entirely under the master analytical scheme program.

Thus, column techniques are most useful in cases where they have already been defined for specific applications and where their incorporation into the master analytical scheme would require only further validation and delineation of operating parameters.

CHEMICAL DERIVATIZATION

In the analysis of environmental water samples very little attention has been given to developing good derivatization methods for the quantification and identification of polar organic compounds. This may in part be due to the nature of the analyses. Most extraction methods have preferentially concentrated hydrophobic substances and experimental procedures have often been designated to be as simple and as rapid as possible thereby minimizing both the need for and desirability of chemical derivatization techniques. Acetylation or esterification using diazomethane have been the preferred methods when derivatization is performed. However, due to the complexity of the sample mixture and the natural matrix interferences, quantitative reproducible results are not often achieved.

The important criteria for incorporating chemical derivatization into the master analytical scheme should include (a) quantitative and reproducible derivative yields for as many compounds as possible over a wide range of concentrations, (b) low sample contamination and artifact formation, (c) insensitivity of the derivatization reaction to sample matrix, and (d) formation of derivatives with characteristic mass spectral fragmentation patterns for compound identification and quantification.

The exact derivatizaiton technique which should be employed depends on sample concentration and fractionation procedures used on the original water matrix. It appears that even the most universal derivatization technique has given better results with homogeneous samples in the simple matrix, suggesting that extensive fractionation would at least optimize the derivatization step. Ideally, fractionation schemes should be employed in the master analytical scheme that separate compounds according to functional group class as well as remove inorganic ions and high molecular weight organic interferences. If this can be achieved, then optimum derivatization conditions could be applied to each compound class to give quantitative and reproducible results.

GAS CHROMATOGRAPHY

With the gradual acceptance of high resolution gas chromatography as a routine analytic tool, the analysis of complex mixtures are becoming more facile with a reduction in the effort necessary for sample purification prior to analysis. Nevertheless, with the more complex samples such as municipal, industrial, and energy waters, high resolution gas chromatography by itself may be insufficient for resolving all of the constituents which are present.

A review of the gas chromatographic conditions utilized for the analysis of organics in environmental waters reveals that a relatively few phases have emerged as the most frequently applied materials. These are: nonpolar phases such as SE-30, OV-1, and OV-101, semi-polar phases such as OV-17, QF-1, and mixed phase combinations, and the polar phase Carbowax 20M.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY/COMPUTER TECHNIQUES

Instrumentation

There are several criteria which GC/MS instrumentation must meet for the Master Analytical Scheme. The Master Analytical Scheme requires a total overall recovery for any compound of at least 40%. A procedural detection limit of 0.01 μg/l is desired. This translates to an instrumental detection limit of 4 ng assuming a one liter sample size. The GC must be able to accommodate a variety of columns both packed and capillary. The GC also requires accurate control of oven programming since analyses must be reproducible if quantitative information is to be extracted. Operating in the capillary mode requires appropriate injection systems to accommodate split or splitless modes.

Although the upper mass limit for most organic compounds of interest is about 500 daltons, the mass spectrometer must be capable of acquiring data up to approximately 1,000 daltons since many derivatized species and brominated species have molecular weights approaching 1,000 daltons. The resolution of the instrument must be such that the peaks in the upper mass range are resolvable. At minimum resolution of 1,000, a mass 1,000 must be obtainable.

The data system, as a minimum, needs to be capable of spectral acquisition and processing as well as generation of reconstructed gas chromatograms and selected ion plots. The system must also have the capacity for long-term storage of data.

Commercial GC/MS/DS systems that meet the above criteria for the Master Analytical Scheme are available from many manufacturers.

Instrument stability is a factor which must be defined for the GC/MS/DS system under the Master Analytical Scheme. Stability encompasses both mass drift and changes in sensitivity between high and low masses.

Computer hardware and software packages are available with the following capabilities: (1) generation of reconstructed gas chromatograms; (2) generation of selected ion plots from full scan data; (3) background subtraction; (4) storage of all scans from a run; and (5) hard copy capability. Also, many instruments have real time displays, simultaneous data acquisition and data processing, and long-term data storage as well as computer control of the mass spectrometer. Primary differences are a matter of degre more than concept.

There are a number of ionization processes available; however, only two have been widely used in water analysis, i.e., electron impact ionization and chemical ionization (CI). The electron impact technique has been the most commonly and widely employed (approximately 95% of all mass spectrometry work) of the two forms of ionization. It has been applied to all classes of compounds which are to be addressed by the Master Analytical Scheme.

The most commonly used gases for chemical ionization have been methane and isobutane. Methane and isobutane have been extensively investigated as reagent gases for hydrocarbons, amino acids, alcohols, amines, ketones, esters, miscellaneous nitrogen compounds, carbohydrates, steroids, pesticides, and organometallics.

Another commonly used reagent gas in chemical ionization is ammonia. This reagent gas reacts with esters, acids, ketones, aldehydes, alcohols, and hydrocarbons. It has been employed to differentiate between primary, secondary, and tertiary alcohols and to qualitatively assay components and complex hydrocarbon mixtures where attachment occurs with alkenes but not with cycloalkanes. A number of other reagent gases have also been used. Although CI has been extensively used, it suffers from a lack of uniform operating parameters in and between laboratories. It is envisioned as an auxillary technique in water analysis rather than as a major mode of ionization.

Negative ion mass spectrometry has not been generally accepted as an analytical technique due to the low yield of ions. Negative ion mass spectrometry can be 10^3 less sensitive than positive ion mass spectrometry. However, recently developed techniques of negative ion chemical ionization have overcome the sensitivity problem for selected compounds. The negative chemical ionization method has proven to be selective; it is most efficient for compound with high electron affinities. Various types of negative chemical ionization techniques have been applied to compounds such as chlorinated aromatics, herbicides, polycyclic chlorinated insecticides, polycyclic aromatic compounds, organophosphorus pesticides, polychlorinated dibenzodioxanes, and aromatic chlorinated pesticides. In the majority of the cases cited, enhancement of sensitivity by a factor of 10^3 over positive chemical ionization techniques has been often observed.

Due to the selectivity of negative ion chemical ionization, its most probable applications for the Master Analytical Scheme lie in the area of detection of specific compound classes, e.g., halogenated compounds, rather than as a general tool.

Field ionization is another ionization technique, but it has not had extensive application in water analysis.

Finally, one technique that may hold great promise for an analytical program of this type is high resolution gas chromatography/high resolution mass spectrometry.

Identification by Noncomputerized Approaches

Compound identification is one of the two most crucial components of the data reduction process, and it has been the phase of operation most often dismissed in the literature with the phrase "the compounds were identified by mass spectrometry." No mention is generally made of the criteria used for identification, nor has there been an indication of the level of confidence in the identification. Thus, specific criteria need to be delineated under the Master Analytical Scheme that include a step-by-step process that will lead to the identification of a compound. Perhaps it should encompass several levels of certainty of identification depending on time and materials available. Each level should represent a degree of certainty of identification.

Computer Processing of GC/MS Data

Many of the computer software programs reviewed here have been used extensively by GC/MS users throughout the world. Notwithstanding this fact, a critical evaluation of these procedures based on appropriate controlled experiments has not been published. It should, therefore, be emphasized that although the programs mentioned are actually being used daily for practical analytical tasks, the entire field of automated mass spectral analysis must still be considered to be in the experimental stage and the results derived from the use of such techniques cannot be considered as definitive or unequivocal.

Quantitation

Quantitation is considered the second crucial issue that needs to be addressed by the Master Analytical Scheme. The precision and accuracy of a measurement are two very important parameters to be considered when quantitating a substance. For quantification, internal or external standards are normally used. The choice of standards is limited to isotopically labeled compounds or substituted compounds such as fluorinated compounds since they are not in the water sample being analyzed. There must be a minimum of 3 mass units difference between the internal standard ions and the ions from naturally occurring isotopes of any of the unlabeled compounds present in the original water sample. This eliminated ^{13}C isotopically labeled compounds from consideration. The internal standards should obviously elute from the GC at a point different from that of any substance of identifical mass; e.g., d_6-benzene (mass 84) should not elute in the same region as that of the hexenes (mass 84).

Techniques for quantitation of compounds based on mass spectral data can be divided into categories: (a) selective ion monitoring; (b) total ion current; and (c) selected ion plots. The technique of selected ion plots (also known as extracted ion current profiles) has been widely used. A characteristic ion of a compound is extracted from full scan data to obtain quantitative information for the compound. This method appears to have been the most commonly employed technique by investigators who require the quantification of many organics in a single sample.

QUALITY ASSURANCE/QUALITY CONTROL

There is a need for a well-defined quality control (QC) and quality assurance (QA) program during the performance of research projects. One of the serious deficiencies of much of the research which has been performed to date and reported in the literature is the lack of recorded good laboratory practices. The Master Analytical Scheme should strive to incorporate strict QC/QA procedures.

SECTION 3

SAMPLING, PHASE SEPARATIONS, PRESERVATION, AND INTERNAL STANDARDS.

The importance of procedures for collection and preservation of aqueous samples for organic analysis cannot be overemphasized. The value of the analysis as a whole is compromised if the sample being analyzed is not characteristic of the environment under investigation. The sample must be collected so that it is representative of the process or body of water being sampled, and the sample must be presented to preparation and analysis procedures without loss of any of the compounds of interest and without contamination . The choice of methodologies to be employed in collection and preservation of samples must take into consideration the system that is being sampled, the compounds of interest in the sample, and the analytical techniques which will be used to determine these compounds.

COLLECTION

There are two basic procedures used for aqueous sampling: discontinuous or batch sampling and continuous sampling.

Batch Sampling

Batch sampling is probably the most commonly used procedure because it is simple, fast, and requires no specialized apparatus. Usually, the sample container, a bottle or jar, is filled with the aqueous sample and capped. If a sample collected by the batch method is to be analyzed for very volatile organic compounds,(1) the bottle must be filled and capped so that there are no air air pockets into which the compounds of interest can vaporize. Sample bottles are filled to overflowing and then sealed using a Teflon septum and twist cap or crimp top. The twist cap system is generally preferred(2,3) since it does not require specialized equipment as does the crimp top. If headspace analysis(4) is to be used in determining these highly volatile compounds, approximately 1 mL of headspace should remain in the bottles after the samples have been collected. The bottles should be sealed immediately using a Teflon® septum and twist cap.(5) A combined sample collection/storage/purge vessel has been designed for the analysis of volatile organics in sediments(6,7) and biological fluids.(8) During sampling, a narrow-mouth glass bottle containing a Teflon stir bar is partially filled with sample. It is then sealed with a screw cap containing a Teflon-faced silicon septum. During analysis, the purge gas enters the stirred sample through an 18 gauge needle and exits onto a sorbent trap through a second needle. Using this approach, losses of volatile components due to sample transfer are eliminated.

Storage conditions can significantly affect analyte recovery during volatile analysis. For samples sealed using Teflon® septa, losses of components were lowest for samples stored without headspace. If headspace is present, losses are minimized by storing the sample inverted. Apparently volatile organics partition into the headspace and then can permeate through the Teflon® septum over time. A new sampling device for volatiles has been proposed:(9) a hollow Teflon® cylinder with a sampling inlet port and floating plug at opposite ends. As water is pumped into the chamber, pressure forces the plug upward. Since there is no headspace and water may be pumped from below the surface, losses of volatile components are minimized. Slight losses may occur from the sides of the Teflon® plug during prolonged storage. For all techniques for the analysis of volatiles, it is advisable to collect separate samples for replicate analyses .

Batch sampling for the analysis of moderately volatile compounds is generally carried out by simply filling the sample containers with the aqueous sample and sealing them with a Teflon®-(10) or aluminum-lined twist cap. No particular attention is paid to how full these containers are as long as there is sufficient sample for the analysis.

There are significant problems associated with the use of batch extraction techniques. Batch sampling increases the probability of obtaining nonrepresentative samples. Analysis of a sample obtained by batch methods provides information about the system only at the point and time at which the sample is taken. Statements made about the system as a whole based on this information may be inaccurate. Pooling, blending, and dividing a number of grab samples or using depth-integrated batch samplers(1) to obtain a sample which is truly representative requires a detailed knowledge of the flow and transport characteristics of the system, whether it is surface water, waste stream, or industrial effluent.(11,12) For volatile compounds, pooling or blending are unacceptable since significant losses of volatile components may occur during transfer.

Continuous Sampling

An alternative to batch sampling is continuous sampling. With this method, a large volume of water is pumped into a sample reservoir or through a column packed with a sorbent material. The sorbent material is commonly activated carbon, resin, or polyurethane foam. Characteristics and applicability of these materials will be discussed in a later section of this report. Continuous methods allow sampling of larger volumes of water over extended periods of time. Thus, samples collected by this technique are more representative of the system under investigation,(13) and results of the analyses of these samples are not affected by spurious changes in the character of the system under investigation. Additionally, a single time-integrated sample can often be collected and analyzed in lieu of several batch samples to significantly reduce analysis costs.

Ideally, a continuous sample should meet several specific requirements.(14) The sampler must be capable of taking continuous, constant volume or flow proportional samples. Volumes delivered should be precisely controlled, especially if the data will be used to calculate loading.(15,16) For the reduction of losses due to sorption and chemical reactions, all surfaces in contact with the sample should be inert, and contact time of the sample with sampler surfaces should be as brief as possible. Further, in order to reduce losses due to volatilization, samples should not be placed under negative (*i.e.*, below ambient) pressure, such as might occur with a vacuum type sampler or any other sampler elevated above the intake point.(17-19,20) The sampler should deliver the same volume of sample regardless of outlet pressure. Provisions for heating and cooling(21) the collection device are also needed in order minimize losses due to volatilization, sorption, and chemical reactions. It may be desirable for several process streams to be sampled simultaneously (as before and after a waste chlorination tank),(22-24) and since no single collection method--collection in a reservoir for liquid extraction, sorption on macroreticular resins, carbon, foam plugs, etc.--is suitable for all classes of compounds, provision for multiple source sampling should be made.(25)

Several sampler designs have been described for collecting organics on accumulator columns. Garrison _et_ _al_.(26) described a new sampler which uses a pump with Teflon® bellows, glass-ball check valves, and Teflon® intake lines. Stepan _et_ _al_.(27) developed a sampler employing peristaltic pumps to force sample through columns containing XAD resins. Tigwell _et_ _al_.(14) developed a multichannel positive deplacement apparatus for collecting water samples from multiple sources and/or multiple collection devices. Several commercial manufacturers are currently advertising modified versions of their standard composite samplers which use Teflon® delivery lines and glass vacuum chambers.(28-31)

Disadvantages associated with continuous sampling techniques are that it is time-consuming; it requires specialized (and somewhat costly) equipment, and it is difficult to use if there are space limitations at the sampling site. There is also a greater chance of contamination during a continuous sampling procedure since the sample is exposed for longer periods of time and since there are more equipment surfaces which the sample must contact. Samples collected by continuous methods are subject to losses, degradation, and contamination just as those collected batchwise. Losses are particularly significant for more volatile compounds, and it is difficult to add any type of preservative to a sample which has been collected on a sorbent column. Tight seals or refrigeration of columns during shipment and storage minimize losses due to volatility. It has been suggested that compounds adsorbed on solid supports, particularly activated carbon, can undergo chemical changes.(32)

Sample Contamination

A problem which affects both batch and continuous sampled waters is contamination. Cleanliness of the sample containers and cap is very important if contamination of the sample is to be avoided. Procedures for cleaning sample containers prior to use include washing in hot water and detergent and rinsing as follows: three times each with hot tap water and deionized, distilled water, once each with acetone and methanol, and, finally, three times with deionized, distilled water. The glassware is then oven-dried at 110°C for at least one hour.(1,2) Other procedures to minimize this problem of contamination include use of sorbents which have been pretreated to remove residual material, use of very pure chemicals in any preservation steps, and tight sealing of sample containers or columns for shipment and storage. Despite these measures, contamination is likely to occur. Therefore, it is necessary to include a field blank with each set of samples. A field blank is water of known purity which is collected under controlled laboratory conditions and then subjected to the environment of exposure, handling, shipping, and storing along with the samples. In this way, it is possible to identify and quantify compounds in the sample which are due to contamination.

PHASE SEPARATIONS

Environmental waters are not a one-phase system, and, in most cases, aqueous organic contaminants do not exhibit true solution behavior. Rather, the behavior is governed by competitive interactions between phases. In order to develop a comprehensive, non-biased scheme to adequately sample and analyze water matrices, it is necessary to know the identity of competing phases, their nature, their effect on organics in aquatic ecosystems, and their experimental behavior during analysis. Three phases--particulates, colloids, and oils--will be considered in this light.

Particulates

The term particulate has never been well defined and is usually considered in an operational context. The USGS definition is the most generally accepted: particulates are considered as any species that will be retained on a 0.45 μ filter.(33)

Obviously, this characterization does not specify the nature of the particulate species, and any material from inert sands to very adsorptive clays and biological matter is included. This large variation in physicochemical properties makes it almost impossible to predict the effect of particulates on aqueous organics and may be responsible for large anomalies in experimental results.

Adsorption is the predominant interaction in aqueous solutions. Results from partition studies with PNAs in defined water systems suggest several trends:(34) a) adsorption is a reversible process; b) adsorption is closely related to the molecular volume of the organic species; c) kinetics of surface adsorption and desorption is rapid; d) adsorption is a temperature dependent process; e) adsorption is greater on organic particulates than on inorganic clays; and f) below the solubility limit, partition coefficients are independent of concentration. Representative partition coefficients range from 2×10^4 to 3×10^3 for benz[a]pyrene and anthracene, respectively. Other studies have shown that adsorption when a slow process actually involves surface uptake followed by pore diffusion.(35) This latter mechanism is the rate-limiting step during desorption and the kinetics of this process should be considered when designing organic extraction procedures.

Although it is generally felt that organics associated with particulate matter are unavailable for biological interaction, there is actually little evidence to support this conclusion. Organic-particulate interactions are important in determining both sedimentation and transport processes.(36) Since adsorption is a reversible process, transported particulate organics may become solubilized in their new environment. Finally, the chemical reactivity of adsorbed organics is not well characterized. But it could be postulated that since many water treatment plants chemically treat water prior to coagulation or filtration, associated organics will become transformed or chlorinated during these processes.

During organic analysis, particulates are usually removed either before or during the organic isolation procedure. By removing them prior to extraction, only soluble organics would be measured during experimental analysis. The second approach attempts to measure organic presence in the water column, but the efficiency and reproducibility of various isolation procedures may be seriously affected by the nature and levels of particulates present.(37) For example, accumulator columns adsorb only soluble organics, but particulates may be trapped in the packing and subsequently eluted; or, as already alluded to, the efficiency of solvent extraction techniques becomes time-dependent when particulates are present.

Reproducibility and uncertainty limits for an analytical scheme can be enhanced if particulates are removed prior to isolation, but methods of removal must be carefully evaluated. Filtration is the most common separation technique. Millipore filters give problems with both contamination and adsorption. Filters which are inert to organic solvents are hydrophobic and restrict water permeability; conversely, hydrophilic filters dissolve in organic solvents precluding solvent extraction procedures.(38) Glass fiber filters are compatible with both water and organic solvents, but may provide active sites for chemical reaction. Further, glass fiber filters are not exclusion filters, but rather filter beds: breakthrough can occur to give spurious results.(39) Lastly, sieve filters have been used for some work. They are easily cleaned, extractable, and reuseable; however, sieves may act as a catalyst for artifact formation. For turbid samples, all filters become plugged easily, restricting sample volumes. Centrifugation appears to be the best approach for removing particulates. This method separates according to particle density rather than size. Centrifugation does not involve as many sample manipulations, which should reduce the possibility of sample loss or contamination. Unfortunately, this technique requires equipment which is rather costly. Also, sample volume is restricted by the size of the centrifuge head. It should be remembered that any separation procedure requires several sample manipulations which would make the losses of volatile organics (*i.e.*, bp $\leq$ 150°C) unavoidable.

Colloids

Colloids and high molecular weight organics (*i.e.*, humic and fulvic acids) also provide a matrix for organic interactions. The chemistry of metal association with this phase has been studied extensively, whereas the possibilities for organic associations are only beginning to be considered. Studies with chloesterol, 2,2',5,5'-tetrachlorobiphenyl,(40) DDT,(41) and various other organics have shown that organic matrix effects do occur. Reverse osmosis studies(41) have shown that most organics are better rejected from a matrix containing high levels of colloids and humates; this rejection is attributable to physicochemical interactions. The effect of these organic-organic associations on bioavailability, transport and compound reactivity has not been explored.

Solvent extraction techniques will concentrate all the volatile and semivolatile organics even in the presence of colloids, whereas sorbent columns will only accumulate those chemicals truly in solution. During direct aqueous injection, high molecular weight organics can react with residual chloride to form trihalomethane.(28)

The most feasible method for separating the aqueous and colloid phases is gel permation chromatography. However, if chromatography is performed directly on the water sample, then organics associated with the colloids and high molecular weight materials will be removed with that phase.(40)

Oils

Another example of phase separation in aqueous samples involves oils entrained in industrial effluents, particularly in effluents from alternative energy production processes. Generally, these samples appear to be one phase when they are collected. During refrigerated storage, the dispersed oil droplets coalesce, separate, and form a second phase in the sample container.(43) The formation of this second phase causes several problems. Since many of the compounds of interest in environmental analysis are hydrophobic, they partition preferentially into the organic phase. This effect and the loss of the species of interest from the aqueous matrix become more significant with time until equilibrium is reached. Therefore, sample preparation and analysis procedures must involve this organic layer if they are to provide reliable information about the system under investigation.

The presence of an oil layer in aqueous samples can also lead to problems of foaming and to the formation of stable emulsions during sample workup procedures.* Although these occurrences are not uncommon in water analysis procedures, they are more severe when there is enough oil entrained in a sample, as there often is in energy-related effluents, to cause a phase separation. General techniques for dealing with foaming and emulsions will be treated in subsequent sections of this review.

Procedures for dealing with this type of phase separation are not well developed. There has not been a thorough investigation into methods to prevent formation of this second phase or into the effects that it has on the analytical results. It is important that the analyst be aware of this phenomenon and be aware that it can compromise the analysis.

INTERNAL STANDARDS

In order to assess the degradation of a sample or the loss of compounds of interest, an internal standard or group of standards (marker compounds) should be added. These are best added to the sample in the field at the time of collection, but are usually added in the laboratory.(44,45,46) The marker compounds should be different from any compounds expected to be in the sample but should be chemically similar to the species of interest so that the fate of the standards mimics the biological and chemical fate of the sample analytes during handling, preservation, transportation, and storage procedures. In order to assess the recovery of the compounds of interest by the sample preparation techniques, another compound is added just prior to sample workup. Any marker compound added to a sample should be mixed with the sample for at least 24 h prior to analysis to insure that equilibrium between the aqueous matrix and other phases has been attained. For samples collected batchwise for determination of compounds, the standard is introduced into the sample with a syringe or pipet. The container is sealed, the sample is mixed and prepared for shipment to the laboratory. With samples collected batchwise for the analysis of highly volatile compounds, there are some difficulties. Samples collected for analysis of volatiles should be chilled in ice before the mixture of volatile marker compounds is added. However, this necessitates a time delay between the actual sampling and the addition of the internal standards and capping and recapping of the sample bottle. Both of the events increase the chances of losses and contamination. Therefore, each step involved in adding internal standards to samples for volatile analysis must be done with great care in order to minimize these processes. Preparing internal standards for volatile analysis presents special problems.(47) If the standard is dissolved in an organic solvent, the solvent itself can interfere with subsequent analysis. On the other hand, addition of a neat standard may not provide adequate dissolution or reproducible results. Standards aliquoted in ethanol have been used most often. In the case of samples collected by continuous methods, the internal standards ideally should be metered into the column influent. This should be done in such a way to insure reproducible retention of the marker compounds on the sorbent material.

PRESERVATION

The immediate analysis of an aqueous sample at the collection site would preclude the need for sample preservation; however, this is impractical for most situations. Preservation of organic samples is a very difficult problem with a limited number of techniques available. Additionally, the requirements of many analytical methodologies impose severe restrictions on the preservation techniques which can be used.

Ideally, preservative would be present in the sample container prior to collection and would disperse immediately, stabilizing all parameters (analytes) for an indefinite period of time. The existence of such a preservation technique has not yet been demonstrated and, in fact, may not be possible considering the diversity of organic contaminants (e.g., aromatics, amines, phenols, epoxides, esters, organohalides, saturates and unsaturates, acids, carbonyl compounds, ethers and phosphates) which must be monitored in aqueous samples.

In addition to microbiological degradation, the possibilities for chemical and photodegradation are equally diverse and will be aggravated by the variability of matrix constituents which act as reactants or catalysts. Samples are protected from photodecomposition by using amber glass bottles as sample containers.(48,49)

Chlorination has been one of the most extensively used techniques for the inhibition of biochemical degradation. Unfortunately, free chlorine is also an active oxidizing agent and readily reacts with substituted aromatics (e.g., phenols, anilines, styrene) to produce the ring-chlorinated analogs. Such electrophilic aromatic substitutions can be further catalyzed in many raw source water matrices by the presence of metal ions, particularly Fe^{+2}. In the presence of radical initiators (e.g., light), free radial chlorination can also produce the corresponding benzylic or allylic chlorides (e.g., from alkylbenzenes). Thus, the use of chlorine as a preservative is not appropriate when trace levels of aromatic species are to be analyzed. In addition, the presence of free chlorine must be avoided in situations where organohalides are of interest as potential analytes. Sodium thiosulfate,(3,50) sodium sulfite,(51) potassium ferrocyanide,(52) and ascorbic acid(58) are commonly used to quench free chlorine in water samples.

Alternate sterilization techniques and biocides reported for environmental matrices include: 1) mercuric chloride;(54) 2) formalin or hexachlorophene;(55) and 3) sodium hydroxide, sulfuric acid or copper sulfate-phosphoric acid.(56) It should be noted that up to 20 mg/L of mercuric chloride was found recently to be ineffective in preventing biodegradation of ^{14}C-acetic acid in sediment, whereas the addition of 2% methylene chloride provided a recovery of approximately 90% after 14 days.(57) Unfortunately, the use of methylene chloride as a preservative is not appropriate in samples to be analyzed for volatile organics. An alternative to chemical preservation is to seal the sample container and store the sample at as low a temperature as possible.

The industrial use of biocides has been considerably more widespread than use in environmental analysis. Control of microbiological growth (*i.e.*, algae, fungus, bacteria) has been a major concern in the pulp and paper industry and in industrial cooling water systems. For this reason, the effectiveness of a large number of commerically available biostatic and biocidal agents was reviewed by J. H. Conkey in 1969.(57) Of particular value is the author's listing of over 300 agents, their active ingredients and the concentrations (*i.e.*, of the commercial formulation) required to inhibit growth of two strains of bacteria and two strains of fungus prevalent in pulp and paper mill systems and products. Approximately 20% of the biocides reviewed by Conkey (1969) contain organomercury, organotin or organoarsenic compounds. These, however, have limited applicability due to their high toxicity. Another 11% of the listed formulations contain chlorinated phenols (e.g., pentachlorophenol or its sodium salt). Unfortunately, these chlorophenol-based biocides could interfere with analysis of similar compounds in aqueous samples. Of the remaining biocides, many were found to be relatively ineffective (*i.e.*, required > 1000 ppm inhibiting concentration) against one or more of the test species. Although the specific relationship between biocide effectiveness against the test species versus the variety of microorganisms found in surface and drinking water matrices has not been defined, it would appear that agents with the broadest biocidal activity would offer the greatest measure of overall protection in the preservation of volatile aromatics. In addition, the biocidal agents must also meet the following criteria: 1) compatibility with analytical methodology, 2) nonreactivity towards organic analytes, and 3) low relative toxicity to the analyst.

A list of preservative agents with possible applicability to the analysis of organics in water is given in Table 1. Although these preservatives represent only a small percentage of the biocides found in the literature, a majority had to be eliminated based on their failure to meet one or more of the criteria discussed previously.

Another process which can compromise the integrity of an aqueous sample is adsorption of the organic components onto the glass walls of the sample container. This problem is minimized by the addition of a nonpolar solvent such as isooctane (Appendix A), methylcyclohexane(63), or methylene chloride (Appendix A) to the sample container before it is sealed in the field. It is possible to avoid problems associated with preservation and shipment of

Table 1. CANDIDATE PRESERVATIVES

Biocide	LD_{50} (mg/kg)[a]	Commercial Formulation(s)	% Active Component	Inactive Component(s)	Inhibiting Conc. (ppm)[b]	Supplier(s)	Reference
Methylene bisthiocyanate	161	-- Cytox 3522 Slime-Trol RX-32P	-- 10% 7%	-- dispersants solid binder	(water insoluble) 12.5 - 100 0.25 - 1.25	Tridom American Cyanamide Betz PaperChem	57 58 59
Sodium 2-mercaptopyridine-1-oxide	250	Omadine	40%	water	<.25 - 250	Olin Tridom	57 60
2,2'-Dihydroxy-5,5'-dichlorodiphenylmethane	1000	G-4 (Panacide)	(sodium salt)	water	30 - 900[c]	Givaudan Pfaltz & Bauer	
2,3-Dimethyl-1,3,5,2H-tetrahydrothiodiazine-2-thione					50 - 650	Nalco Chem Service	57 61
8-Hydroxyquinoline	1200	Busan 25				Buckman Aldrich	57
1,1'-Hexamethylenebix[5-(p-chlorophenyl)biguanide]	2000	Chlorhexidine	100%	--	10 - 50	Sigma	62
n-Dodecylguanidine hydrochloride	700	Cytox 2013 Cytox 2050	33%	2-propanol (15%)	0.6 - 30 20 - 60	American Cyanamide American Cyanamide Chem Service (acetate salt)	59
Sodium dimethyldithiocarbamate + Disodium ethylenebisdithiocarbamate	500	Slime-Trol RX-34	15% 15%	dispersants	0.4 - 5.0	Betz Paperchem Bodman	57 59 61
Sodium dimethyldithiocarbamate + Sodium 2-mercaptobenzothiazole	3000	Vancide 51	27.6% 2.4%	water	500 - 1000	R. T. Vanderbilt Alco	57 59 61
Phenylmercuric acetate	30	--	100%	--	2[d]	Aldrich	57

[a] Oral-rat or mouse.

[b] Concentration of formulation recommended by manufacturer.

[c] Range of inhibiting concentrations against Aerobacter aerogenes given by Conkey (1969) for all commercial formulations listed.

[d] Inhibiting concentration given by Conkey (1969) for pure material against Aerobacter aerogenes.

liquid samples by adsorbing the compounds of interest onto carbon, resin, or foam in the field after the sample has been collected by batch techniques.(55) This method has been suggested for the analysis of highly volatile compounds using purge-and-trap techniques.(50)

REFERENCES

1. Bellar, T. A., J. J. Lichtenberg, J. Amer. Water Works Assoc., 28, 739 (1974).
2. Trussell, A. R., M. D. Umphres, L. Y. C. Leong, R. R. Trussel, in Water Chlorination, R. E. Jolley, ed., Ann Arbor Science, Ann Arbor, MI, 1975, p. 543.
3. Brass, H. J., M. A. Feige, T. Holloran, J. W. Mellow, D. Munch, R. F. Thomas, ACS 173rd National Meeting, New Orleans, LA (1977).
4. Dow Chemical, Louisiana, Method QA-466, 1972.
5. Dressman, R. C., E. F. McFarren, J. Chromatogr. Sci., 15, 69 (1977).
6. Spies, D. N., Determination of Purgeable Organics in Sediment Using a Modified Purge and Trap Technique, U. S. Environmental Protection Agency, Edison, NJ, 1980.
7. Zweidinger, R. A., A Comprehensive Method for the Analysis of Volatile Organics on Solids, Sediments, and Sludges, Monthly Technical Progress Report No. 8, EPA Contract No. 68-03-2994, April 1981.
8. Pellizzari, E. D., Chemical and Statistical Analysis of Toxic Substances in Environmental Media-Total Exposure Assessment Methodology, Monthly Technical Progress Report No. 9, EPA Contract No. 68-02-3679, January 1982.
9. Proposed Protocol for Priority Pollutants, U.S. Environmental Protection Agency, August 1978.
10. Moseman, R. F., H. L. Crist, T. R. Edgerton, M. K. Ware, Arch. Environ. Contam. Toxicol., 6, 221 (1977).
11. Feltz, H. R., J. K. Culbertson, Pestic. Monit. J., 6, 171 (1972).
12. Hall, J. R., M. N. Wass, R. A. Solomon, ACS 173rd National Meeting, Miami, FL, September 1978.
13. Lewis, R. G., NBS Special Publication No. 442 (1976), p. 9.
14. Tigwell, D. C., D. J. Schaeffer, and L. Lauden, Anal. Chem., 53, 1199 (1981).

15. Schaeffer, D. F., K. G. Janardan, Bion. J., 20, 215 (1978).

16. Schaeffer, D. J., H. W. Kerster, K. G. Janardan, Environ. Mange., 4, 187 (1980).

17. Lauch, R. P., "A Survey of Commercially Available Automatic Wastewater Samplers," EPA 600/4-76-051, U.S. Environmental Protection Agency, Cincinnati, OH, 1976.

18. Huibergise, K. R., J. H. Moser, "Handbook for Sampling and Sample Preservation of Water and Wastewater," EPA 600/4-76/049, U.S. Environmental Protection Agency, Washington, DC, 1976; National Technical Information Service, 1976, PC-259 946.

19. Shelly, P. E., "Sampling of Water and Wastewater," EPA 600/4-77/039, U. S. Environmental Protection Agency, Cincinnati, OH, 1977; National Technical Information Service, 1977, PB-272 664.

20. Barkley, J. J., "Water Pollution Sampler Evaluation," Army Medical Bioengineering Research and Development Laboratory, Fort Detrich, MD, 1975.

21. Lin, P. C. L., "Thermal Analysis of the ISCO 1680 Portable Wastewater Sampler," EPA 600/4-80-033, U. S. Environmental Protection Agency, 1980.

22. Chian, E. S. K., F. B. DeWalle, "Analytical Methods for Priority Pollutants in Municipal Sewage and Sludge," Water Pollution Control Federation, 1979, Abstracts 52nd Annual Conference of the Water Pollution Control Federation Oct 7-12, Session 25.

23. DeWalle, F. B., D. A. Kalman, C. Perera, E. S. K. Chian, "Priority Pollutant Removal Efficiencies in POTW's as Related to their Physical-Chemical Properties," Water Pollution Control Federation, 1979, Abstracts 52nd Annual Conference of the Water Pollution Control Federation Oct 7-12, Session 8.

24. DeWalle, F., E. Chian, "Presence of Priority Pollutants in Sewage and Their Removal in Sewage Treatment Plants. First Annual Report to U. S. Environmental Protection Agency," University of Washington, Seattle, WA, 1979.

25. Janardan, K. G., D. J. Schaeffer, S. M. Somani, Bull. Environ. Contamin. Toxicol., 24, 145 (1980).

26. Garrison, A. W., J. D. Pope, A. L. Alford, C. K. Doll, NBS Spec. Publ. No. 519, 65 (1979).

27. Stephan, S. F., J. F. Smith, U. Flego, Water Res. 12, 447 (1978).

28. Tigwell, D. C., D. J. Schaeffer, Patent Application, 1979.

29. Thurman, E. M., R. L. Malcolm, G. R. Aiken, Anal. Chem., 51, 1979 (1979).

30. Schaeffer, D. J., W. B. Glave, S. M. Somani, K. G. Janardan, Bull. Environ. Contamin. Toxicol., 25, 569 (1980).

31. May, W. E., S. P. Wasik, D. H. Freeman, Anal. Chem., 50, 997 (1978).

32. Sproul, O., D. W. Rychman, J. Water Pollut. Control Fed., 33, 1188 (1961).

33. Mancy, K. H., Water Pollution Analysis, Ann Arbor Science Publishers, Inc., 1972, 476 pp.

34. Herbes, S. E., Water Research, 11, 493 (1977).

35. Kirchoff, S., U. S. Environmental Protection Agency, Quarterly Highlights, Athens, GA, 1978.

36. Southworth, G., ASTM 2nd Ann. Symp. on Aquatic Toxicology, Cleveland, OH, October 1977.

37. Acheson, M. A., R. M. Harrison, P. Perry, R. A. Wellings, Water Research, 10, 207 (1976).

38. 1978 Millipore Catalogue and Purchasing Guide, Cat. No. MC 177/μ, Millipore Corp., Bedford, MA, 1977, 96 pp.

39. Gelman Membrane Filtration Products, New Dimensions, PB 322 (5/75) Gelman Inst. Co., Ann Arbor, MI, 1975.

40. Hassett, J. P., M. A. Anderson, ACS 173rd National Meeting, Division of Environmental Chemistry, Miami Beach, FL, September 1978.

41. Hindin, E., P. J. Bennetti, S. S. Naraijanan, Water and Sew. Works, 116, 466 (1969).

42. Pfaender, F. K., R. B. Jones, A. A. Stevens, L. More, J. R. Hass, Environ. Sci. Technol., 12, 438 (1978).

43. Pellizzari, E. D., Identification of Components of Energy Related Wastes and Effluents, U. S. Envrionmental Protection Agency, EPA 600/7-77/004, 500 pp., January 1978.

44. Ewing, B. B., E. S. K. Chian, J. C. Cook, C. A. Evans, P. K. Hopke, E. C. Perkins, Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters, U. S. Environmental Protection Agency, EPA 560/6-77-051, July 1977, 45 pp.

45. Lin, D. C. K., D. A. Contos, R. L. Foltz, V. R. Goff, T. L. Hayes, P. P. Kelly, S. V. Lucas, B. S. Mackey, B. A. Petersen, L. E. Slivon, R. Warren, S. C. Watson, U. S. Environmental Protection Agency, Project No. 68-03-2548.

46. Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants, U. S. Environmental Protection Agency, April 1977.

47. Pellizzari, E. D., Preliminary Assessment of Halogenated Organic Compounds in Man and Environmental Media, U. S. Environmental Protection Agency, Contract No. 68-01-4731, July 1978.

48. Ginn, T. M. F. M. Fisher, Pestic. Monit. J., 8, 23 (1974).

49. John, E. D., G. Nickless, J. Chromatogr., 138, 399 (1977).

50. Trussel, A., M. Umphres, L. Leong, A. Trussel, submitted to J. Amer. Water Works Assoc.

51. Henderson, J. E., G. R. Peyton, W. H. Glaz, in Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science , Ann Arbor, MI, 1976, p. 105.

52. Kopfler, F. C., R. G. Melton, R. D. Lingg, W. E. Coleman, ibid., p. 84.

53. Kissinger, L. D., J. S. Fritz, J. Amer. Water Work Ass., 69, 435 (1976).

54. Sutton, C. J., A. Calder, Environ. Sci. Technol., 8, 654 (1974).

55. Shultz, D. J., J. F. Pankow, D. Y. Tai, D. W. Stephans, R. E. Rahtbun, J. Res. U. S. Geol. Survey, 4, 247 (1976).

56. Carter, M. J., M. T. Huston, Environ. Sci. Technol., 12, 309 (1978).

57. Conkey, J. H., Tappi, 12, 2311 (1969).

58. Friend, P. L., W. K. Whilekettle, Devel. Industrial Microbiol., 21, 123 (1980).

59. McCoy, J. W., Microbiology of Cooling Water, Chemical Publishing Company, 1980.

60. Nerchof, R. A., C. A. Barley, C. Patouillet, P. J. Hannan, Arch. Environ. Contam. Toxicol., 8, 355 (1979).

61. Cappeline, G. A., J. G. Carroll, S. D. Shcuss, Power, 121, 56 (1977).

62. Saxena, J., E. Nies, New Approaches to the Preservation of Contaminants in Water Samples, EPA 600/4-79/007, U. S. Environmental Protection Agency, Cincinnati, OH, 59 p.

63. Neure, J. A., J. Amer. Water Work Assoc., 69, 60 (1977).

64. Bellar, T. A., J. J. Lichtenberg, The Determination of Volatile Organic Compounds at the μg/l Level in Water by Gas Chromatography, U. S. Environmental Protection Agency, EPA 670/4-74/009, 1974, 95 pp.

SECTION 4

TECHNIQUES FOR SAMPLE COMPONENT ISOLATION AND/OR CONCENTRATION

STATIC HEADSPACE ANALYSIS

Principles of the Technique

Static headspace analysis is a method for determining volatile compounds in liquids or solids by measuring vapor phase components which are in thermodynamic equilibrium with the sample of interest in a closed system. For aqueous systems, the distribution of sample components between water and gaseous phases depends upon their water solubility and vapor pressure at the equilibration temperature. For example, compounds with a high vapor pressure and low solubility will preferentially partition into the vapor phase.

Headspace analysis is most often used in conjunction with gas chromatography and will be considered exclusively in this sense. For quantitative analysis, peak area (F_i) is the parameter measured and at relatively low pressures is proportional to the partial vapor pressure (P_i) of the volatile component i in the headspace, the relationship is known as Henry's Law

$$F_i \sim P_i \qquad (1)$$

$$F_i = \bar{C}_i P_i \qquad (2)$$

where $\bar{C}_i$ is a constant dependent upon the chromatographic detector. The partial vapor pressure P_i is generally expressed as

$$P_i = P_{oi} X_i \gamma_i \qquad (3)$$

where P_{oi} is the vapor pressure of i, X_i is the mole fraction of i, and γ_i is the activity coefficient of component i dissolved in the sample. Substituting equation (3) into equation (2) shows the relationship between peak area (F_i) and the above parameters.(1)

$$F_i = C_i P_{oi} X_i \gamma_i \qquad (4)$$

For a given sample, with a fixed chromatographic system (X_i and C_i are constant), peak area and, hence, sensitivity may be varied by changing either P_{oi} or γ_i. Vapor pressure (P_{oi}) may be increased by increasing the equilibration temperature, whereas the activity coefficient is most effectively increased by adding electrolyte to the solution, *i.e.*, "salting out."

In static headspace analysis, equilibration is performed in a sealed glass container at a constant temperature. Equilibration time depends upon the sample volume and equilibration temperature and, in most cases, even with large samples does not exceed 60 minutes.

After equilibration, a volume of headspace is injected onto the chromatographic column using a gas tight syringe(1,2,3) or a gas sampling loop.(4-7) Since the sample is a gas, a heated injection port is unnecessary making this technique well suited for heat labile compounds. Usually packed column gas chromatography has been used for analysis; however, adaptation to high resolution capillary columns with no loss in quantitative precision and a significant improvement in retention time accuracy and chromatographic separation has been reported.(8-10) A shorter analysis time has also been reported using capillary columns.(8)

Accurate quantitative analysis for the static headspace technique depends upon the calibration procedure. Since the partition coefficient of the solute in the equilibrated gas-liquid system is a function of its activity coefficient, calibration solutions should closely approximate the sample matrix. A standard addition method was developed to calibrate unknown samples.(8,11,12) As an alternative, hydrocarbons in water were quantitated using multiple equilibrations of the sample with equal volumes of gas.(13,14) Each gaseous extract was analyzed by GC and analyte concentrations calculated by extrapolating the relationship between the peak areas and the number of equilibrations.

Quantitative headspace analysis can be a very accurate procedure. However, good reproducibility depends upon two factors, namely, exact temperature control during equilibration, and a reproducible method for transporting and injecting the headspace sample into the gas chromatograph. Results with a commercial headspace sample accessory have given precisions of 0.8% as a coefficient of variation.(15,16) A precision of ±5% was reported for the analysis of halocarbons in drinking, surface, and wastewater samples.(17)

When a vessel for headspace analysis is selected, consideration should be given to several points.(18) First, if a rubber septum is used, the exposed surfaces should be kept as small as possible to minimize effects due to dissolution and diffusion. Second, the volume of the headspace vessel should not be too large compared with that of the sample, since under certain circumstances, depending on Henry's Law constants, it might result in total evaporation of the component being analyzed into the gas phase. The assumptions made for quantitative analysis would no longer be satisfied, since the sample would not then be in equilibrium with the vapor phase. Third, to facilitate effective and rapid temperature equilibration, the volumes of the headspace analysis vessel and the headspace itself should not be too large. Finally, care must be taken to ensure that the glass is sufficiently strong to withstand high pressures if necessary. A variety of sample vessels have been used including serum vials,(18,19) separatory funnels,(12) and modified volumetric flasks.(8)

The use of a semi-automatic headspace sampling and gas chromatographic injection system has also been reported.(20) The conventional method for withdrawing headspace gas with a syringe through an elastic rubber septum may cause adsorptive losses onto the walls of the syringe as well as volatility losses through the pierced septum. Adsorptive losses as large as 80%(21) have been reported. As an alternative, samples were injected onto the gas chromatograph using an eight-port gas sampling valve. Equilibration was carried out directly on the chromatographic column. A reproducibility of better than 1% was obtained in both peak heights and peak ratios.(21)

A salting-out method has been used to improve headspace analysis.(18) A quantity of 1.2 g sodium sulfate was transferred to a 2 mL sample. After the vial was sealed, the solution was mixed on a mechanical shaker for 5 min. Then it was allowed to equilibrate for 3 min at 60°C and a 1 mL sample of headspace gas was analyzed. A 4- to 7-fold increase in gas chromatographic peak height for sulfides, carbonyls, esters, and alcohols at the 1 ppm level was reported.

The effect of temperature, salt concentration, and pH on equilibrium vapor pressure was studied for a set of four polar compounds.(22) Increasing the equilibration temperature from 30° to 50°C and the salt concentration to 3.35 M sodium sulfate improved partition coefficients from 0.004 to 26 for methyl ethyl ketone, 0.003 to .073 for nitroethane, 0.0008 to .044 for butanol, and 0.0003 to 0.013 for dioxane. The effect of "salting out" was significantly larger than the temperature effect.

Limits of Detection

Detection limits for static headspace analysis depend upon: compound type, GC detector, conditions for equilibration and preconcentration techniques. Table 1 summarizes reported detection limits under a variety of test conditions.

Compound Types and Recovery Data

Any compound which will give a vapor pressure over its aqueous matrix can be analyzed via static headspace analysis. Obviously, the higher the vapor pressure, the more suitable the technique. Low molecular weight, low boiling point, hydrophobic compounds are best suited.

It was reported that vapor phase partitioning for the following chemical classes followed the order: alkanes > olefins > cycloalkanes > aromatics.(23) Within each chemical class, an increased vapor partition was observed as the molecular weight increased. A study of a series of n-alkane standards showed that even C_{22} could be detected, although its boiling point is greater than 300°C.(15) Headspace analysis can selectively separate nonpolar volatiles from more water soluble alcohols and acids. With salting-out and sufficiently high equilibration temperatures, water soluble compounds including methanol, ethanol, acetone, and methyl ethyl ketone are also amenable to analysis. However, use of elevated temperatures during equilibration may prevent the analyses of heat-sensitive compounds.

Compounds with high solubility in water and very low vapor pressures can also be determined by the headspace method if they can be derivatized by a suitable reagent prior to analysis. Hexafluoroacetone was analyzed by converting it to fluoroform via treatment with potassium hydroxide.(24) A 140 mL sample was allowed to react with 0.35 M of potassium hydroxide for five hours at 85°C. A 5 mL aliquot of headspace gas was removed and analyzed by GC/FID. A detection limit of 10 ppb was obtained. Trifluoroacetic(25) and trichloroacetic acids(26) have been analyzed as their methyl esters after derivatization with dimethylsulfate.

The headspace technique is promising in the determination of sulfur-containing compounds. Conventional methods of adsorption, extraction, and chromatography have encountered difficulties because of instability and ease of oxidation of these compounds. Application of phase equilibrium without any special treatment permits determination of mercaptans, sulfides, and disulfides in aqueous solution at concentrations as low as 1 ppb.(21)

Table 1. DETECTION LIMITS FOR STATIC HEADSPACE ANALYSIS

Compound or Compound Class	Equilibration Condition	Pre-Concentration	Detector	Detection Limit	Reference
Chloroform	90°C, 45 min no salt	None	ECD	1 ppb	2
Sulfides, carbonyls, esters	Na_2SO_4	None	FID	10 ppb	19
Halogenated aliphatics	3.35M Na_2SO_4, 50°C	None	ECD	1 ppb	22
Methanol	Na_2SO_4	None	FID	1 ppm	19
Methanol, ethanol, acetone	70°C, Na_2SO_4	Distillation	FID	4 ppb	3
Methyl ethyl ketone	70°C, Na_2SO_4	Distillation	FID	8 ppb	3
Halogenated aliphatics	80°C, no salt	None	FID	1-5 ppb	26
Hydrocarbons	___[a]	None	FID	100 ppm	13
Hydrocarbons	40°C, no salt	None	FID	2 ppb	11
Benzene	40°C, no salt	None	FID	100 ppb	8
Chloroform	0.1$\underline{N}$ $Na_2S_2O_3$, 50°C	None	FID	1.5 ppb	27
Vinyl chloride	___	None	FID	5 ppb	28
Hexachloroacetone, hexafluoroacetone	___	KOH hydrolysis	FID	10 ppb	29

[a] Exact conditions unknown.

Since static headspace analysis depends upon partitioning and high recoveries are not expected, recovery data are usually not given. Detection limits are a more representative parameter for judging the efficacy of this technique.

Sample Type

The headsapce technique is applicable to all water types, biological fluids, food substances, and some solid samples. A number of investigators have used this technique to determine hydrocarbons in various environmental solutions.(8,11,12,13,14,30) The analysis of halogenated hydrocarbons in drinking water has also been reported.(22,27) Hexachloroacetone and hexafluoroacetone were detected in industrial wastewaters using headspace analysis after alkaline decarboxylation.(25) Ethanol,(10) vinyl chloride,(28) acetaldehyde,(31) and volatile anesthetics(32) were analyzed in blood and various other biological matrices. In addition, headspace analysis has been applied to the analysis of beverages(33,34) and other foodstuffs.(35)

Advantages and Disadvantages

Static headspace analysis is a simple, reproducible, rapid technique for measuring volatile organic compounds in water. Analysis times ranging from 20 to 45 minutes have been reported. The headspace method is capable of high throughput since large numbers of samples can be analyzed simultaneously. Further, the problem of solvent interference is eliminated.

The range of molecular weights, boiling points and solubilities greatly limits the number of compounds that can be directly analyzed by the headspace method.(32,35) Due to their solubility, low molecular weight compounds can only be detected at high concentrations or at reduced pressure. This is also true for alcohols.

An insufficient distinction between the haloforms actually present in water and those that are formed from precursors during headspace analysis has been reported. These haloforms either decompose in the aqueous matrix or they are too(29) soluble for headspace analysis.

In the analysis of acetic acid, acetaldehyde, methanol and hexafluoroacetone, headspace analysis was less satisfactory than direct analysis.(35) Improved sensitivity with adsorption columns prior to gas chromatographic analysis has been observed.(21) Reliable results were obtained with concentrations at 0.1 ppb for ketones, amines, alcohols and sulfides.

Conclusions

Due to its simplicity, short performance time, and good sensitivity, static headspace analysis is routinely used for determining volatiles in both solids and liquids. In the study of polymers, headspace analysis has been used for measuring monomer content and for detecting trace levels of organic solvents. Headspace analysis techniques are highly adaptable to water analysis and are used for the determination of volatile hydrophobic compounds. However, the purge and trap technique has proven to be more desirable in terms of sensitivity and accuracy.

PURGE AND TRAP

Principles of the Technique

The most widely used method for isolating volatile organic materials (boiling point <200°C) from water is to purge the sample with prepurified gas, collect the stripped materials on a sorbent trap, and analyze the trapped compounds by thermal desorption followed by gas chromatography or gas chromatography/mass spectrometry. Alternatively, for samples which tend to foam, the sample headspace may be purged instead of the sample itself.

Removal of organic compounds from water by sparging with an inert gas is frequently referred to as volatile organic analysis (VOA) or purge and trap. The technique depends upon partitioning of the compounds between the aqueous and gaseous phases. This partitioning is a function of water temperature, gas-water interfacial area, and the water solubilities (<2%), volatilities (<200°C), and aqueous activity coefficients of the test compounds. In addition, the partition rate depends on the flow rate and total volume of the purge gas.

The glass apparatus in which the sample is contained during analysis may be of two basic types: either a vessel with the purge gas inlet beneath the surface of the sample or a vessel with the inlet above the sample surface. The former case may be one of many designs but, generally, the gas is diffused into tiny bubbles immediately prior to passing upward through the sample. Alternately, the gas may be introduced as large bubbles.(36) One of the first and most well-known purging devices was designed by Bellar and Lichtenberg.(37,38)

A number of studies have compared alternate stripping vessels with the Bellar and Lichtenberg (B&L) device.(39,40,41) Generally, the alternate vessels were the same size or of larger capacity (up to 500 mL) than the B&L vessel which can accommodate about 10 mL. The larger vessels were evaluated in an attempt to reduce detection limits during VOA. All of the large purge vessels were less efficient than the B&L design especially for polar low molecular weight compounds. A miniaturized B&L apparatus (sample volume: 1 mL) actually improved recoveries for a fixed volume of purge gas.(42) Another study of stripping vessel geometry concluded that recoveries were enhanced by increasing the path length of contact between purge gas and sample vessel.(43) During headspace stripping the gas passes over the sample surface rather than passing through it.(44,45) Recoveries are slightly lower than for direct purging but problems associated with foaming are eliminated.

The assembled VOA apparatus consists of a container with a purge gas inlet, a device for regulating sample temperature, and a purge gas outlet through a sorbent cartridge. Although most analyses involve transport of the sample to the laboratory, a device has been developed for stripping the sample in the field.(46,47)

The cartridge is composed of material with a high affinity for organic compounds, and preferably, a low affinity for water. The affinity of a sorbent cartridge for any analyte may be measured as its breakthrough volume. This parameter is the volume of gas, which, when passed through the sorbent cartridge, elutes 50% of a discrete sample component introduced onto the leading end of the cartridge. Essentially, the sorbent cartridge is acting like a gas chromatographic column. Breakthrough volumes at various temperatures of some representative compounds have been reported for Tenax GC®.(48) In addition to temperature, breakthrough volume is a function of sorbent type and cartridge geometry.

Tenax GC® is the most commonly used trapping material. It is thermally stable, contains few background contaminants, provides few sites for irreversible adsorption, is chemically inert, and has a low affinity for water. Its major drawback is its low affinity for a number of very volatile organic compounds including vinyl chloride and epoxyethane.(48) Alternate sorbents such as Porapak Q, silica gel, activated carbon, Carbosieve B, and Ambersorb have also been employed. EPA Method 624(49) for the analysis of volatile organics currently uses a silica gel/Tenax trap.

Sample volumes vary from 0.5-1000 mL depending upon the type of sample and concentration of the substances to be determined. Gas flow rates range from 20-200 mL/min and purge times from a few minutes to several hours depending, again, upon the sample concentration and the appropriate breakthrough volume for the target analyte on the sorbent cartridge.

There are a number of considerations involved in determinating purge temperature. Even though maximum stripping occurs at 90-98°C, these elevated temperatures may cause problems with condensation on the trap material, artifact formation, and thermal decomposition. Furthermore, samples which tend to foam do so to a greater degree at higher temperatures. For these reasons, analysis of low molecular weight, hydrophobic compounds is performed at ambient temperatures. Compounds with boiling point less than 200°C and aqueous solubilities less than 2% are amenable to this type of analysis. Elevated temperature purge and trap techniques have been reported for a number of volatile polar organic compounds.(39,42,49,50) Recoveries of many of these compounds improved significantly with the addition of salt to the aqueous solution prior to analysis.(42,50)

Analytes trapped on the sorbent cartridge are introduced into the chromatographic system using thermal desorption. At this point test components may be either focused in a cryogenic trap(51) or transferred directly to the GC column. For packed column analysis the latter approach is generally used. The purge and trap technique can be performed with the cartridge directly on-line to the gas chromatograph and detector system as specified by EPA Method 624(49) for volatile organic analysis. Several commercial instruments are available with this arrangement. Alternately, the purge operation can be performed off-line with the cartridge later desorbed onto the chromatographic column. The on-line technique provides significantly cleaner sample blanks. Repetitive desorption of a single trap also avoids problems with cleaning and storing cartridges. Cartridges exposed off-line can be stored without significant sample loss which may facilitate the scheduling of sample analysis.(48) In addition cartridges purged off-line can be desiccated prior to desorption to remove water trapped during the purge procedure.(48)

For the separation of volatiles, particularly halogenated species, both capillary(52,53,54,55) and packed columns have been used. Chromosorb 101, Carbowax 1500 and 20M, SE-30 and OV-101 are the most frequently used liquid phases for GC analyses. The current EPA Priority Pollutant Protocol(49) specifies a 6 foot glass column packed with either Carbowax 20M or SP-1000 on Carbopack B. Fused silica capillary columns with bonded phases have become popular for all GC analysis including the analysis of volatile compounds. However, the use of an on-line purge and trap system interfaced to a capillary column causes several difficult problems.

During capillary column chromatography the sample components must be introduced onto the column as a sharp band to avoid deteriorating chromatographic resolution. This may be achieved by cryotrapping using either a cryofocusing unit(51) or by cooling a small portion of the capillary column to liquid nitrogen temperatures.(56) Unfortunately, the volume of water collected on the trapping material is often large enough to cause freezing during the focusing procedure. The use of a water cooled condenser(57) or a condenser tube(52) to remove water from the gas stream prior to the sorbent cartridge has been reported. A dry purge of the sample cartridge to remove water after the load operation has also been reported.(58) Other researchers have split the gas stream after desorption to minimize the amount of water entering the chromatographic system.(55) However, this significantly decreases method sensitivity.

Even with high resolution chromatography, extremely complex mixtures may require pre-columns for separation of organic compounds into classes. For example, lanthanide chelating agents have been suggested for isolating oxygenated compounds. Each of these classes could then be analyzed separately.

Limits of Detection

As previously mentioned, purging of organic compounds from water depends upon the water temperature, the area of water in contact with the purge gas and the solubility and volatility of the compounds. The sample temperature cannot be raised substantially above 95°C before significant quantities of water condense on the sorbent trap. Water adsorbed by the trap will interfere with desorption and GC analysis but, at least for Tenax, does not affect breakthrough volumes.(59) The gas-water interfacial area is limited by the glass frit porosity which will readily permit passage of the purge gas. Therefore, for optimum circumstances, the detection limit is controlled, with respect to sample work-up, primarily by the solubility of the compound(s), the breakthrough volume of the specific adsorbent, the sample volume purged and the sensitivity of the GC detector. The limit has been assigned at approximately 0.1 ppb(57) for halogenated compounds using ECD detection. Detection limits using full scan mass spectrometry for detection range from 1 to 10 ppb with a 5 mL sample size.(49,60) Detection limits can be reduced an order of magnitude or more if selected ion monitoring is employed.

Compound Types and Recovery Data

Purge and trap is applicable to analysis of compounds described as volatile. This operational definition includes any substances which can be purged from water in a gas stream and generally implies compounds with boiling points less than 200°C. Insofar as the purge itself cannot specifically isolate certain compounds or selectively discriminate against others, the separation of sample components must be accomplished by gas chromatography.

The recovery data (Tables 2 and 3) show a number of significant facts. For ambient temperature purge the recoveries are nearly quantitative for many compounds, particularly halogenated materials for which the technique is most widely used; the recovery is generally not a function of concentration between 1 and 200 ppb and compounds up to a molecular weight of 260 can be efficiently determined.

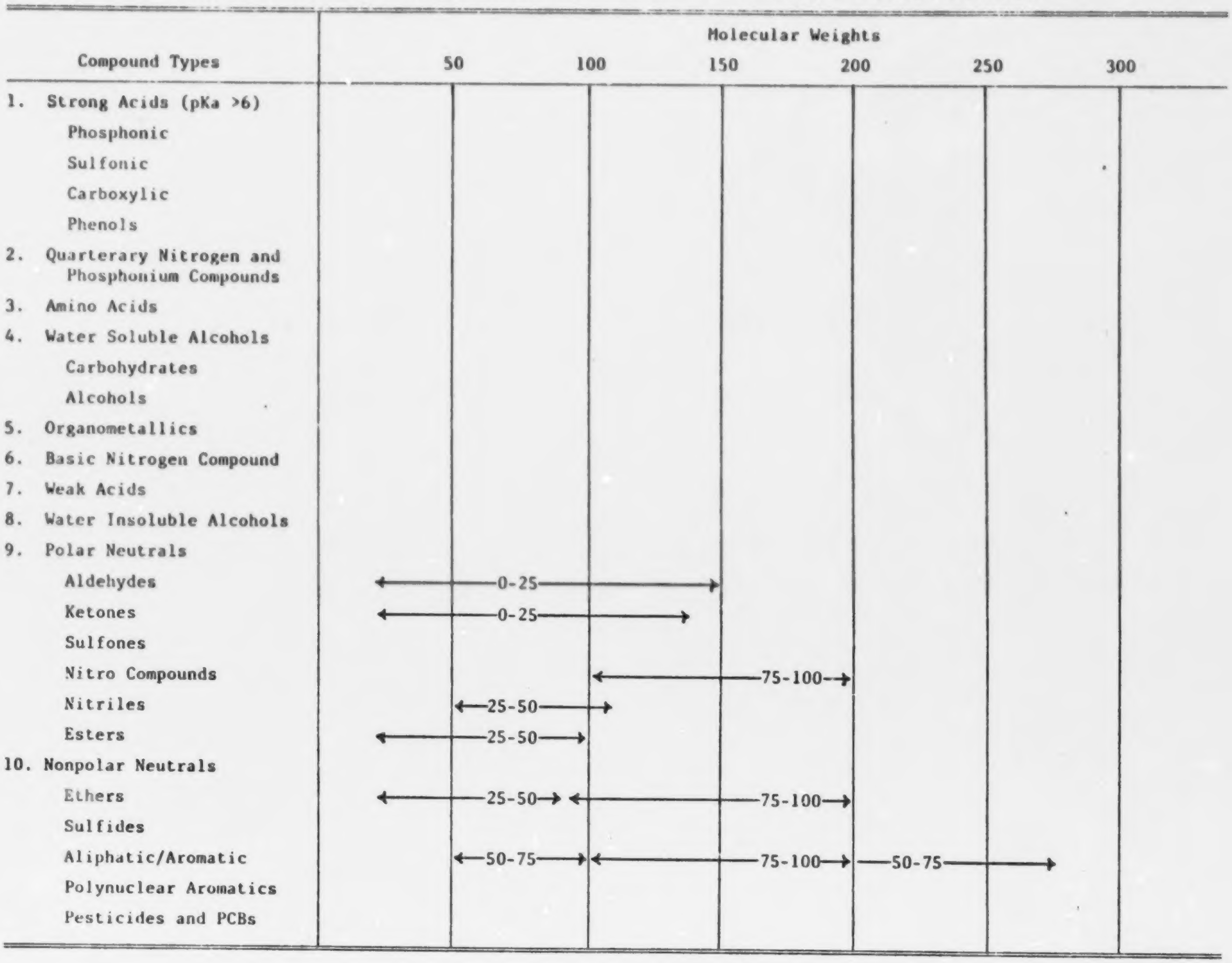
Water solubility is a dominant factor in determining purge efficiency. This is reflected in the lack of a trend between purge efficiency and increasing molecular weight. Elevated temperature purge and trap techniques have been used to analyze some of the more water soluble compounds.(39,42,49,50)

Radiolabeled recovery studies on energy-related samples summarize the recovery of volatile organic compounds in a manner consistent with other findings.(56) At 30°C, purging was found to be quantitative for compounds with boiling points less than 210°C and less than 2% aqueous solubility and for compounds with boiling points less than 150°C with an aqueous solubility of less than 10% in water. Compounds with high aqueous solubilities are recovered only to the extent of approximately 10%.

Sample Types

Volatile compounds in drinking water, ground waters, innumerable surface waters and wastewaters, including municipal, industrial and energy wastes have been determined by purge and trap. In principle, any aqueous sample can be analyzed by this method, the only limitation being that the sample

Table 2. PERCENT RECOVERIES BY AMBIENT TEMPERATURE PURGE AND TRAP



Compound Types	Molecular Weights (50, 100, 150, 200, 250, 300)
1. Strong Acids (pKa >6)	
Phosphonic	
Sulfonic	
Carboxylic	
Phenols	
2. Quarterary Nitrogen and Phosphonium Compounds	
3. Amino Acids	
4. Water Soluble Alcohols	
Carbohydrates	
Alcohols	
5. Organometallics	
6. Basic Nitrogen Compound	
7. Weak Acids	
8. Water Insoluble Alcohols	
9. Polar Neutrals	
Aldehydes	←0-25→
Ketones	←0-25→
Sulfones	
Nitro Compounds	←75-100→
Nitriles	←25-50→
Esters	←25-50→
10. Nonpolar Neutrals	
Ethers	←25-50→ ←75-100→
Sulfides	
Aliphatic/Aromatic	←50-75→ ←75-100→ 50-75→
Polynuclear Aromatics	
Pesticides and PCBs	

Table 3. PERCENT RECOVERIES BY ELEVATED TEMPERATURE PURGE AND TRAP

Compound Types	Molecular Weights						
	50	100	150	200	250	300	
1. Strong Acids (pKa >6)							
Phosphonic							
Sulfonic							
Carboxylic							
Phenols							
2. Quarterary Nitrogen and Phosphonium Compounds							
3. Amino Acids							
4. Water Soluble Alcohols							
Carbohydrates							
Alcohols	←25-75→						
5. Organometallics							
6. Basic Nitrogen Compound							
7. Weak Acids							
8. Water Insoluble Alcohols		←75-100→					
9. Polar Neutrals							
Aldehydes	←50-75—	←75-100→					
Ketones	←—	—75-100—	→				
Sulfones							
Nitro Compounds		←—	—75-100→				
Nitriles		←—	—75-100→				
Esters	←50-75→	←—	—75-100→				
10. Nonpolar Neutrals							
Ethers							
Sulfides							
Aliphatic/Aromatic							
Polynuclear Aromatics							
Pesticides and PCBs							

not present an uncontrollable foaming problem when purged. Several methods have been used to control foaming, including headspace purging,(44,45) foam traps,(41,48) sample dilution,(60) and antifoam agents.(61,62)

Advantages and Disadvantages

The applicability of purge and trap to nearly any aqueous matrix make it one of the more versatile techniques for determining volatile and semi-volatile compounds in water. Only compounds with high water solubilities cannot be efficiently recovered using ambient temperature purge and trap. The facility of the method, enabling simultaneous work-up of several samples by a single operator, reduces the cost of analysis per sample. In addition, the apparatus itself is relatively inexpensive and is readily available. Because the entire sample is introduced during analysis, detection limits are significantly lower than extraction techniques.

The purge and trap technique shows few problems with sample contamination or artifact formation. In fact, comparative studies on the recovery of chloroform with direct aqueous injection (DAI) showed significantly lower recoveries using VOA. It was hypothesized that chloroform was produced in the heated injection port using DAI.

Although mass balance studies using ^{14}C-labeled compounds have shown that the purge efficiency of chloroform, carbon tetrachloride, chlorobenzene and bromobenzene from the sample is quantitative, recovery studies using similar compounds have indicated an overall method recovery of approximately 80-90%.(64,65)

Recovery of compounds by purge and trap has been found to depend on the sample matrix. Samples which contain appreciable quantities of surface active materials tend to foam and therefore cannot be effectively purged. Foaming can be controlled by use of a foam trap or in severe cases the headspace purge technique can be employed. High levels of particulates also limit compound recovery.

Conclusions

The purge and trap method is being widely applied to the analysis of halogenated hydrocarbons, primarily in drinking water. In addition considerable effort has been made in improvement of purge apparatus design, particularly for special sample applications. Since purge and trap is the recommended EPA method for measuring volatile priority pollutants,(49) it is probably used more than any other isolation procedure.

The methods used for purging and headspace analysis have been compiled in Table 4. Diagrams of the various pieces of apparatus are also shown (Figures 1-11).

CLOSED-LOOP GAS STRIPPING ANALYSIS (GROB TECHNIQUE)

Principles of the Technique

Examination of several techniques for analysis of volatile organics in water, including solvent extraction, adsorption on sorbent columns and gas stripping shows that gas stripping is significantly more efficient than the other methods for this group of analytes. However, it is limited to compounds of fairly high volatility.(106) A method developed to include gas stripping in a closed-loop system greatly enhances the sensitivity due to a larger sample volume. It also broadens the applicability due to a greater volatility range of determinable organic compounds.

Basically, the closed-loop gas stripping technique (or more commonly called "Grob Technique" after its originator, Kurt Grob) involves continuous gas stripping of water samples followed by trapping on a small activated carbon filter. Using the Grob Method, this can be done by either stripping at 30°C using the headspace gas to purge the sample, or stripping with water vapor by boiling the sample in a closed-loop system.(107-110) A modified version purges the aqueous sample rather than the sample headspace.(111,112) The continuous purge and trap apparatus is constructed entirely of glass or glass and stainless steel to minimize surface contamination.

For ambient stripping, a water sample of 0.5-2.0 L is carefully introduced into a 1 or 5 L glass bottle equilibrated at 30°C, and connected to the closed-loop system. An adsorbent filter constructed of 1.5-5.0 mg heat-activated wood charcoal collects organics in the stripping loop. Stripping is initiated at 1.0-2.5 L/min for 1-3 hours by activation of a stainless steel bellows pump. During the process, stripping gas is warmed to approximately 40°C just prior to the carbon filter to minimize adsorption of water vapor and hence restriction of flow through the filter.

Stripping with water vapor is performed in a 6 L round-bottomed flask filled with 5 L of water and connected to a closed-loop system which permits recycling of the steam. The entire system is vented only through the charcoal adsorbent filter which is slightly heated to prevent condensation. The temperature of the sample is raised to the boiling point as rapidly as

Table 4. SUMMARY OF PURGING TECHNIQUES

Class[a]	Apparatus[b]	Water Type	Compound[c] Types	Sample Volume (mL)	Trap Sorbent	GC Column	Comments	Reference
P + T	P - 2	drinking	volatiles	500	Tenax	-[d]	95°	66
P + T	P - 1	drinking	volatiles	500	-	Chromosorb 101 Tenax	95°	12
P + T	P - 2	drinking	volatiles	500	Tenax	-	95°; 30 min K_2FeCN to reduce Cl_2	15
P + T	P - 3	any	-	-	Tenax	-	Automated system (Hewlett-Packard)	67
H - P	-	alcoholic beverages	volatiles	250	Poropak Q	Carbowax/Ionax/ Gas Quart		68
H - P	P - 4	distilled	polar organics	100	Tenax	-	60°, He, 200 mL/min, 20 min.	38
P + T	P - 1 & P - 4	waste	priority pollutants	10,100	Tenax	Carbowax 1500	H - P and P + T precision comparable	36
		sediments sea water	HC HC	750	Tenax	SE-30 (SCOT)	Sensitive at ppb level 70°, 150 mL/min, 2 h	69
P + T	P - 1 (modified)	surface	purgeables	5	Tenax	Carbowax	90°, He, 20 mL/min, 20 min, 1 ppb sensitivity	70
H - P	-	waste	aldehydes HHC	500-1500	-	OV-101 (WCOT)	40-93% recovery, 10 ppb 70°, 90 min.	43
	P - 1 (Tekmar)	water & wastewater	HHC	-	-	Carbowax 1500	Recovery <50 ppb, 110°	71
P + T	P - 1	drinking surface ground waste	volatiles	5	Tenax	Tenax	Foam trap	37
H - P	1 L-roundbottom	drinking	volatiles	700	Tenax	Emulphor ON 870	95°, He, 60 min.	72,73
		drinking	HHC volatiles			SF-96; Isepal CO 880	95°, attempt to correlate water and blood levels	74
P + T	P - 1 (modified)	drinking	HHC	140	Tenax	Tenax	25°, 20 mL/min, 15 min. Recovery 90% $ChCl_3$ after 100 min. NORS Study	75
P + T	P - 5	energy waste	S,N,O,HC+ aromatics	-	Tenax	OV-101 (SCOT) Carbowax 20M (SCOT)		76,77, 78,79
P + T	P - 1	ground	volatiles	-	-	-	Teflon Bailer for sampling	80
P + T	P - 3	surface drinking water	HHC		Tenax	Carbowax 20M		81
P + T	P - 3	any	volatiles	200	-	-	<1 ppb detection	66
P + T	P - 1	mun. & ind. waste	volatiles	-	-	-		82
H - P	Erlenmeyer	distilled, ind. waste	volatiles	5,20	-	-	25°, 1 L (min., 15 min) 1 ppb detection	App. A[e]

(continued)

Table 4 (cont'd.)

Class[a]	Apparatus[b]	Water Type	Compound[c] Types	Sample Volume (mL)	Trap Sorbent	GC Column	Comments	Reference
H - P	-	distilled, ind. waste	volatiles	<1000	-	-	Efficiency vs. emp. efficiency vs. ionic strength	83
H - P	gas wash bottle	distilled mon. & ind. waste	amines	100-200	Chromosorb W coated w/Cu II	Penwatt 223/NaOH	60°, 1 h, air, 300 mL/min, 10% morpholine recovery	App. A
P + T	glass jar	PVC bottled mineral	HHC	1000	activ. carbon/ cryogenic	-		84
P + T	P - 1	drinking	aromatics	1000	3% Dexsil 300 and Tenax	Tenax	90°, N_2, 30 mL/min, 15 min.	85
P + T	P - 1	surface distilled	vinyl chloride	5	Silica gel, Carbosieve-B	Chromosorb 101	10 min, 20 mL/min	86
P + T	P - 6	surface drinking ind. waste	volatiles HHC	1000-2500	Tenax	Emulphor ON 870 (WCOT)	70°, 40-80 mL/min, 1-3 h	87
P + T	-	drinking waste	volatiles	-	-	-		88
P + T	P - 9	drinking	volatiles	250	none	Carbowax 20M	20°, 100 mL/min, 30 min. detection limit 0.1-60 ppb	89
P + T	-	drinking ind. waste	HHC	-	-	-		90
P + T	-	surface drinking	HC, HHC	[illegible]00	-	VAV-98		91
P + T	-	general	oxyheterocycles nitriles sulfides HC HHC Halo. ether alcohols aldehydes ketones acids	-	-	-	IERL Level 2	92
P + T	P - 1, P - 2	drinking	volatiles HHC	5 or 500	Tenax	-	detection from 0.01-10 ppb, compare P + T with DAI	93
P + T	fritted cylinder	drinking	volatiles	5	-	Chromosorb 101	detection from 0.1-10 ppb Recommend: 75-95%	94
P + T	-	drinking	HHC	-	-	Tenax	Comparison of P + T with DAI	95
P + T	VOA	any	PP	5	Tenax	-	No mention of foaming	96
P + T	P - 1	distilled drinking	-	-	-	Poropak Q	Comparison of P + T with DAI	51
P + T	P - 1	drinking laboratory	HHC	-	-	-		App. A

(continued)

Table 4 (cont'd.)

Class[a]	Apparatus[b]	Water Type	Compound[c] Types	Sample Volume (mL)	Trap Sorbent	GC Column	Comments	Reference
P + T	-	surface ground drinking	volatiles	-	-	-		App. A
P + T	P - 1	surface waste	-	-	-	-	foaming, poor precision	App. A
P + T	-	-	volatiles	-	-	OV-101		App. A
P + T	-	-	HC	-	-	-		App. A
P + T	P - 3	drinking surface ind. waste	-	-	-	-		App. A
P + T		mun. waste	PP	-	Carbopack & Carbowax	SP-2250		App. A
P + T		river	-	250	-	-		App. A
P + T	P - 1	drinking ground surface	HHC solvents	-	Tenax	-		App. A
P + T	P - 1 (Tekmar)	potable surface ind. waste	haloforms	-	-	capillary		App. A
P + T	-	surface	volatiles amines	-	-	-		App. A
P + T	P - 1	mun. & ind. waste	volatiles	-	-	SF-96 (Capillary)	Foaming not a big problem Tekmar samples	App. A
P + T	P - 1	-	volatiles	-	-	-	95-105% recoveries detection limit, 1 ppb	App. A
P + T	P - 1	energy waste chlorinated waters	haloforms	-	-	-		App. A
P + T	P - 1 (Tekmar)	drinking	haloforms HHC	-	Tenax	SP-2100 (WCOT)		App. A
P + T	P - 1	-	PP	-	Tenax	Carbowax 1500		App. A
	-	energy drinking	aromatics haloforms	-	-	OV-101 (WCOT)	ozonalysis vs. chlorination	App. A
P + T	P - 1	waste ground surface drinking	PP	-	-	SP-1240 DA OV-17	emulsion problems	App. A
P + T	P - 1	-	volatiles	-	-	-	reduce sample size for foaming, use syringe to transfer to P + T vessel	App. A
P + T	P - 1	surface drinking	volatiles	5-100	Tenax	-		App. A

(continued)

Table 4 (cont'd.)

Class[a]	Apparatus[b]	Water Type	Compound[c] Types	Sample Volume (mL)	Trap Sorbent	GC Column	Comments	Reference
P + T	P - 1 (Tekmar)	distilled	volatiles HHC	-	2/3 Tenax + 1/3 Silica Gel	SF-96 (WCOT)	1-19% precision	97
H - P	P - 4		PP	120	Tenax	-	60°, 200 mL/min 20-25 min 1000 mL flask best All parameters studied.	98
P + T	-	sewage sludge	PP	-	-	-	blend sample prior to purge	App. A
P + T	-	sewage	PP	-	-	-	no mention of foaming	99
H - P	controlled difussion cell	sage leaves	-	2	Tenax	-	probably not applicable to	100
H - P	bottle	urine	-	100	Tenax	-	100°, He, 120 mL/min., 30 min.	101
H - P	bottle	serum cerebrospinal fluid	-	15	Tenax	-	100°, He, 20 mL/min 3.5 h	101
P - T	P - 10	drinking surface	HHC	100	Tenax	-	90°, He, 25 mL/min, 30 min. blood, urine, sewage foam	64,65, 51
H - P	P - 11	milk	-	50-100	Tenax	-	50°, He, 25 mL/min, 90 min. No foaming	102
P + T	P - 1	drinking	PP	5	Tenax	-	detection limit 0.1 ppb memory effects with Tekmar apparatus. Improved device has no memory effect, can be used in field. Reproducibility, accuracy, and quality control evaluated and discussed.	103

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[a] P + T = purge and trap (through-solution purge).

H - P = headspace purge (dynamic purge of sample headspace).

H = headspace (direct injection of headspace gas).

D - H = distillation followed by headspace sampling.

[b] Numbers refer to figure numbers.

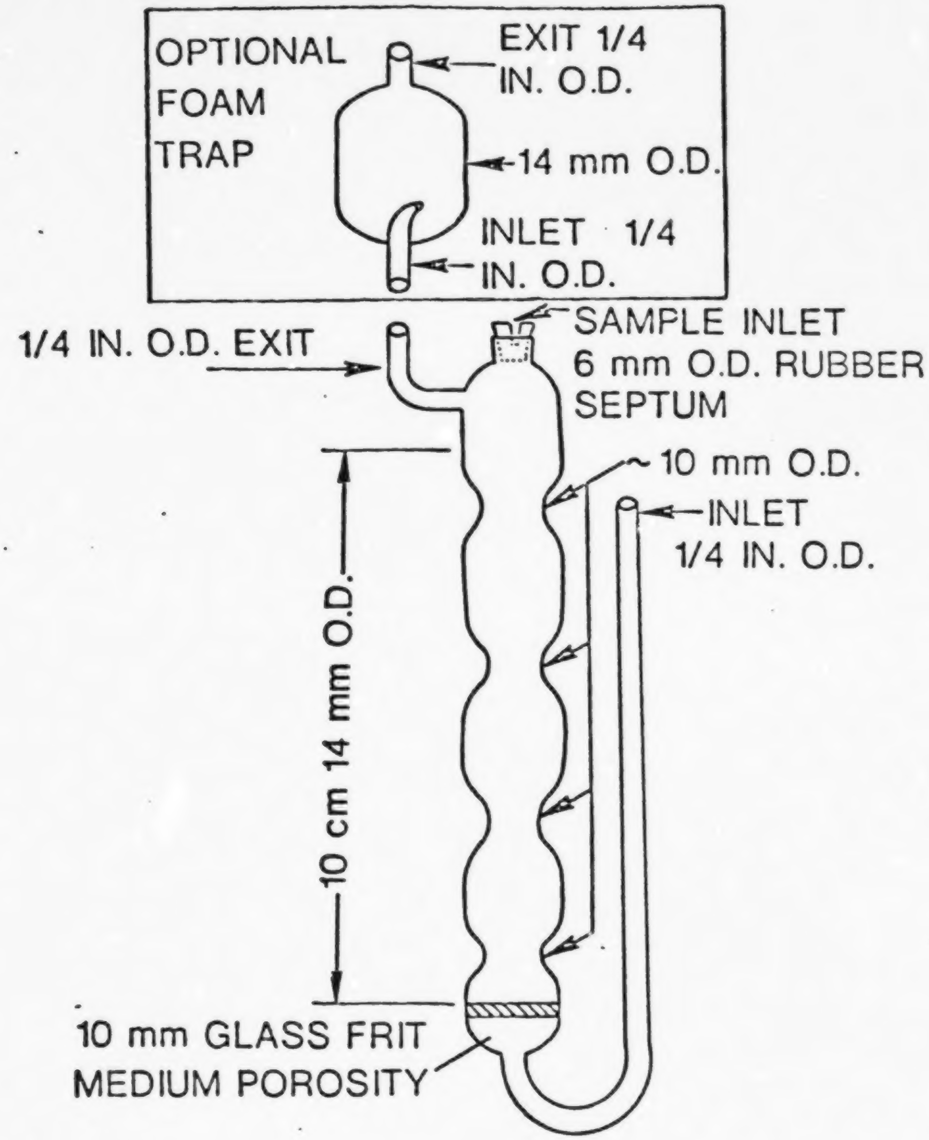
[c] HHC = halogenated hydrocarbons.

H = hydrocarbons.

PP = priority pollutants.

[d] Information not given.

[e] Information obtained through personal communication with individuals listed in Appendix A.



OPTIONAL FOAM TRAP
EXIT 1/4 IN. O.D.
14 mm O.D.
INLET 1/4 IN. O.D.
1/4 IN. O.D. EXIT
SAMPLE INLET 6 mm O.D. RUBBER SEPTUM
~10 mm O.D.
INLET 1/4 IN. O.D.
10 cm 14 mm O.D.
10 mm GLASS FRIT MEDIUM POROSITY

Figure 1. Purging apparatus used in Bellar and Lichtenberg technique.(37)

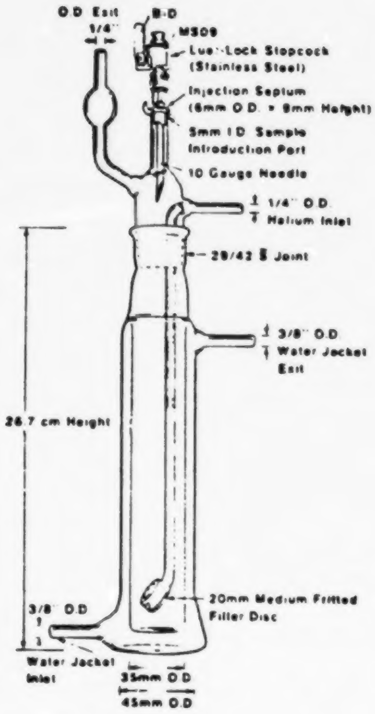

O.D. Exit
1/4"
B-D
MS09
Luer-Lock Stopcock
(Stainless Steel)
Injection Septum
(6mm O.D. × 9mm Height)
5mm I.D. Sample
Introduction Port
10 Gauge Needle
1/4" O.D.
Helium Inlet
29/42 $ Joint
3/8" O.D.
Water Jacket
Exit
26.7 cm Height
20mm Medium Fritted
Filter Disc
3/8" O.D.
Water Jacket
Inlet
35mm O.D.
45mm O.D.

Figure 2. 140 mL VOA purging apparatus.(40)

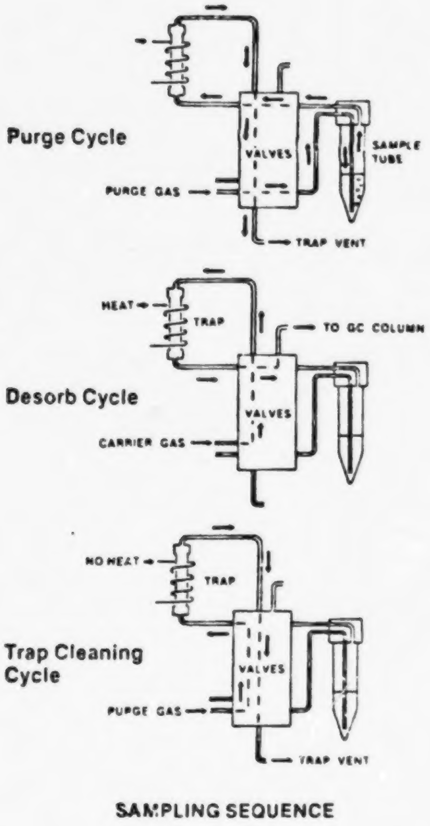

Purge Cycle
VALVES
SAMPLE TUBE
PURGE GAS
TRAP VENT
HEAT
TRAP
TO GC COLUMN
Desorb Cycle
VALVES
CARRIER GAS
NO HEAT
TRAP
Trap Cleaning Cycle
VALVES
PURGE GAS
TRAP VENT
SAMPLING SEQUENCE

Figure 3. Diagram of purge and trap device marketed by Hewlett-Packard. (83) Sample tube is generally a 15 mL centrifuge tube.

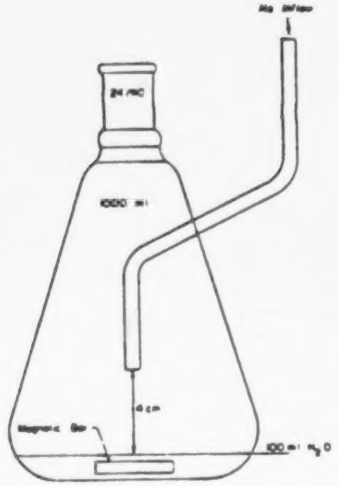

He Inflow
24/40
1000 ml
4 cm
Magnetic Bar
100 ml H_2O

Figure 4. "Stripping Flask" used by Chian and co-workers for headspace purge of water. (38)

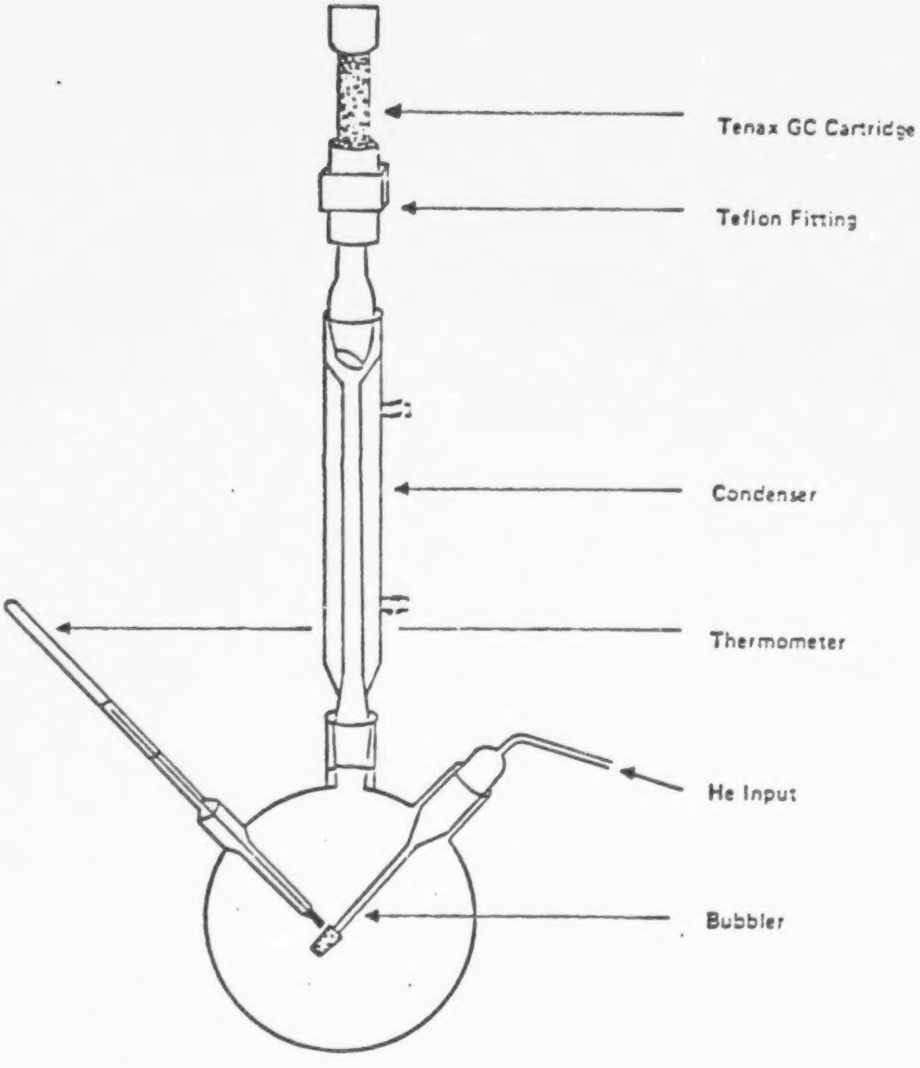

Tenax GC Cartridge
Teflon Fitting
Condenser
Thermometer
He Input
Bubbler

Figure 5.   Apparatus for VOA purge . (56)

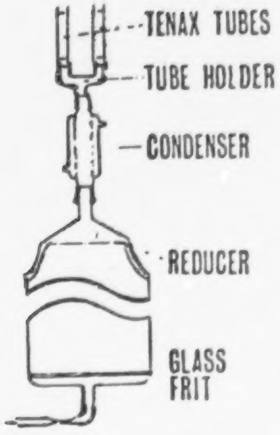

TENAX TUBES
TUBE HOLDER
CONDENSER
REDUCER
GLASS FRIT

Figure 6. Gas-phase stripping device. Dimensions not to scale, sample chamber is 30-75 x 7.0 cm o.d.(87)

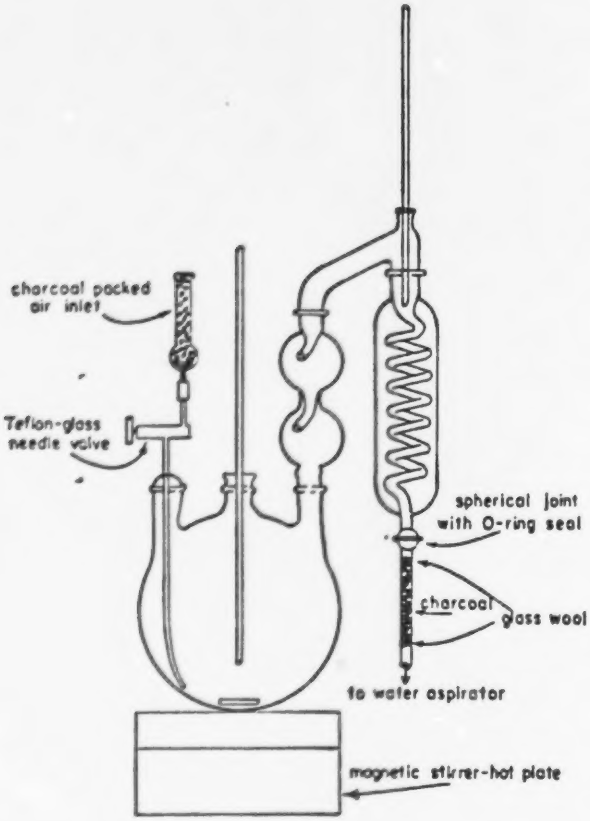
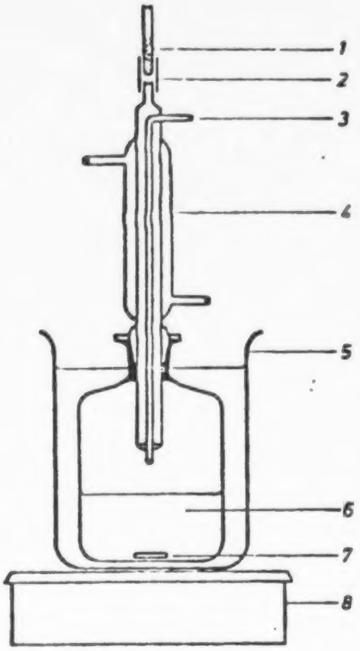

charcoal packed air inlet
Teflon-glass needle valve
spherical joint with O-ring seal
charcoal
glass wool
to water aspirator
magnetic stirrer-hot plate

Figure 7. Distillation - adsorption apparatus. (104)



Aqueous Volatile Sampler

1 Trap-insert with Tenax-GC, 2 Teflon sleeve, 3 Helium inlet, 4 Condenser, 5 Boiling water bath, 6 Sample, 7 Magnetic stirring bar, 8 Hot-plate-stirrer

Figure 8. Aqueous headspace sampler used for purging urine.(105)

Reproduced from best available copy.

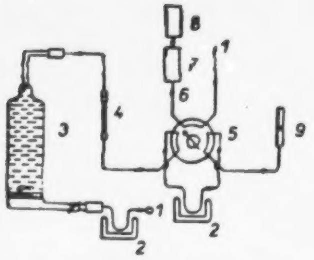


Fig 1 Flow sheet of the apparatus used 1 = Source of inert gas, 2 = freezer, 3 = bubbler, 4 = dryer, 5 = six-way cock, 6 = column inlet, 7 = chromatograph, 8 = mass spectrometer, 9 = integrating flow meter

Figure 9. Purge apparatus used for drinking water.(90)

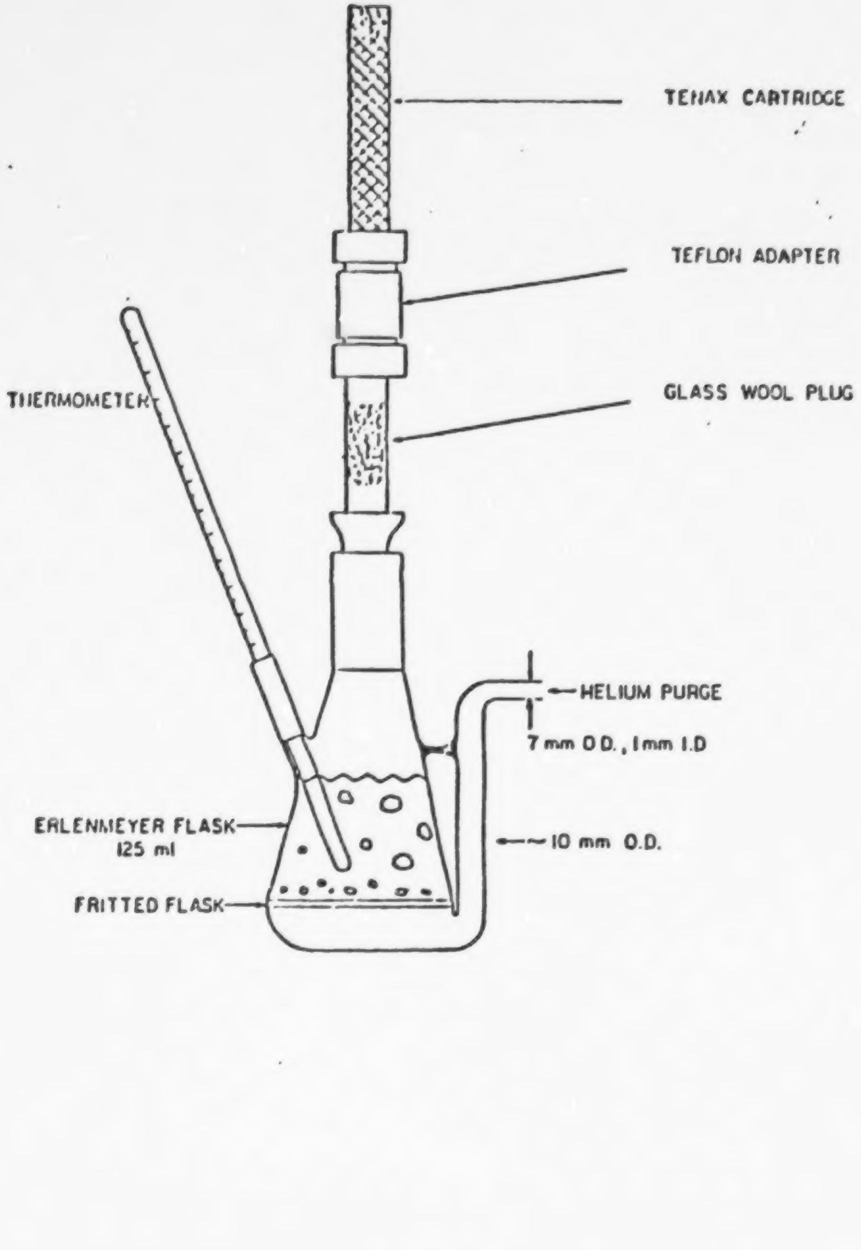

TENAX CARTRIDGE
TEFLON ADAPTER
GLASS WOOL PLUG
THERMOMETER
HELIUM PURGE
7 mm O.D., 1 mm I.D
ERLENMEYER FLASK 125 ml
~10 mm O.D.
FRITTED FLASK

Figure 10. Purge and trap apparatus validated for water samples.(48)

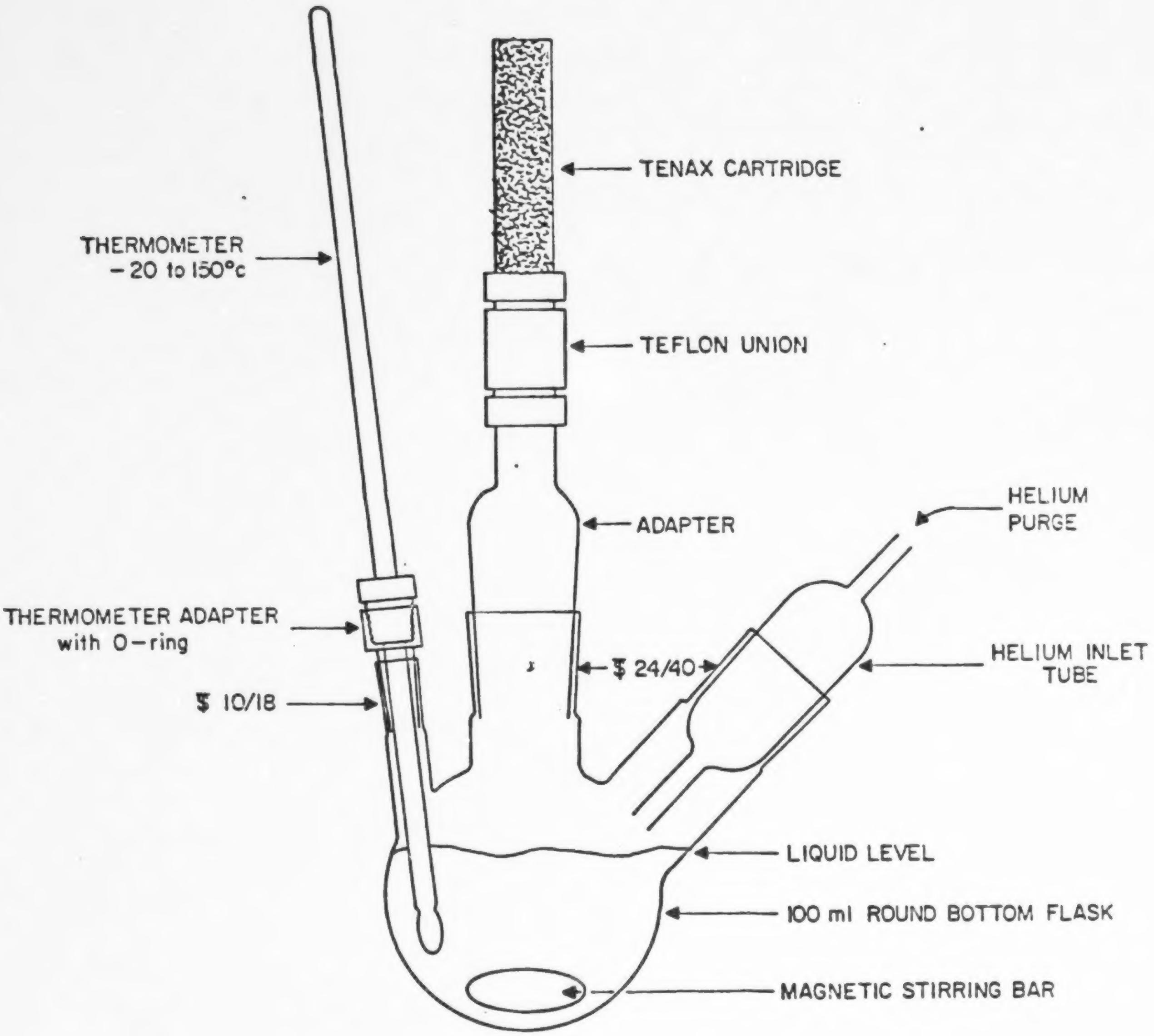

TENAX CARTRIDGE
THERMOMETER
-20 to 150°c
TEFLON UNION
ADAPTER
HELIUM
PURGE
THERMOMETER ADAPTER
with O-ring
$ 24/40
HELIUM INLET
TUBE
$ 10/18
LIQUID LEVEL
100 ml ROUND BOTTOM FLASK
MAGNETIC STIRRING BAR

Figure 11. Headspace purge and trap apparatus validated for purging milk, urine, and blood.(88)

possible by heating with a heating mantle, then maintained at the boiling point with a cartridge heater inserted in the bottom of the flask.

Extraction of the exposed carbon filter can be effected in two ways: if only volatiles are desired, the filter can be analyzed by thermal desorption directly onto the gas chromatographic column.(113) Extraction of less volatile compounds from the filter involves careful elution with 5-15 μL of purified and redistilled carbon disulfide. In cases where heavily contaminated water has been purged, 10-100 μL methylene chloride has been used.(114,115) Component identification as well as quantitative analysis(116) are performed by gas chromatography/mass spectrometry (GC/MS) without further concentration.

Due to the number and diversity of compounds which may be collected on the charcoal filter, glass capillary GC columns are recommended, although packed columns should provide sufficient resolution for clean water samples. UCON LB 550 and Emulphor liquid phases on wall coated open tubular columns (WCOT) have been used for separation of components up to C_{24}.(106,109) Injections of the CS_2 extract were made directly onto the column without splitting.(75) Similar columns coated with SP-2100(116) and SP-1000 have successfully separated relatively non-volatile constituents like phenols, dieldrin and aldrin. Volatile compounds extracted from the exposed carbon filter were determined on SE-52 WCOT columns. Column temperatures were typically programmed from approximately 25-200°C to effect optimum resolution.

No inherent difficulties are associated with mass spectrometric detection in conjunction with closed-loop gas stripping analysis. In every reported instance a mass spectrometer was employed as a detector, presumably because of its utility in identifying components of complex mixtures.

Limits of Detection

The detection limit of the Grob method has been assigned at 0.1 ppt (part per trillion).(106) However, if a 5 L water sample is stripped onto the carbon filter, the filter extracted with 10 μL of carbon disulfide and 2 μL injected into the GC/MS, then a 10 ppt LOD would be achieved assuming 50% stripping efficiency, 100% filter extraction efficiency and a 5 ng LOD for the mass spectrometer.

Compound Types and Recovery Data

Closed loop stripping is essentially a variation of the purge and trap technique, and therefore recovers the same compound classes, but is more effective for high boiling and hydrophobic compounds. It has been compared to purge and trap, batch liquid, liquid extraction, and XAD resin accumulation for organics detected in wastewater samples but recovery data were not given.(117)

The recovery data are presented in Table 5. No data on the relative efficiencies between the gas-stripping and filter extraction processes are yet available, and very few papers report recovery data for the entire procedure.

Sample Types

The Grob method is most applicable to the analysis of drinking, ground and innumerable types of surface waters.(106) Closed-loop stripping is limited with respect to water type by the provision that the sample not foam when purged with an inert gas. Foaming would not only prevent efficient stripping of organics from water but would cause serious and possibly irreversible contamination of the entire closed-loop system. This closed-loop stripping method is thus eliminated for the analysis of many municipal and industrial wastewaters or any waters which contain surfactants or other surface active materials. Many European water laboratories use this method in lieu of the purge and trap technique for volatiles. It has been applied to drinking water utilities,(118) drinking water sources,(114,119) lake water,(120) and seawater(121) by several investigators.

Advantages and Disadvantages

The Grob method is currently one of the most effective techniques available for determining low-level organic compounds in potable waters. This effectiveness is exemplified both in outstanding sensitivity (~ppt) and in molecular weight range of detectable compounds (up to C_{24}). The extraction efficiency is at least comparable to purge and trap for non-polar materials. There is no significant tendency for artifact formation, and, since the purge gas is essentially the headspace of the sample, potential contamination from large quantities of purge gas sometimes employed in conventional purge and trap analysis is avoided.

Table 5. PERCENT RECOVERIES BY CLOSED-LOOP GAS STRIPPING

Compound Types	Molecular Weights <50	50–100	100–150	150–200	200–250	250–300
1. Strong Acids (pKa >6)						
Phosphonic						
Sulfonic						
Carboxylic						
Phenols						
2. Quarterary Nitrogen and Phosphonium Compounds						
3. Amino Acids						
4. Water Soluble Alcohols						
Carbohydrates						
Alcohols						
5. Organometallics						
6. Basic Nitrogen Compound						
7. Weak Acids-(phenols)			0-25	25-50		
8. Water Insoluble Alcohols						
9. Polar Neutrals						
Aldehydes				0-25	50-75	
Ketones			0-25	75-100		
Sulfones						
Nitro Compounds						
Nitriles						
Esters						
10. Nonpolar Neutrals						
Ethers				40-65		
Sulfides						
Aliphatic/Aromatic	0-25	25-50		75-100	50-75	25-50
Polynuclear Aromatics						
Pesticides and PCBs					50-75	

Unlike conventional purge and trap, the necessary equipment for the Grob technique is highly specialized, structurally fragile, quite expensive and not readily available commercially. The analysis itself is time-consuming (3 h strip time), thereby limiting sample throughput. Furthermore, closed-loop gas stripping is not conducive to simultaneous multiple analyses critical to routine water examinations, and, as mentioned previously, cannot be used for samples which tend to foam.

Extracting the charcoal filter is a delicate procedure sensitive to analyst error. The efficiency and reproducibility of the entire method generally depend upon this step and may vary considerably between users.

Other problems associated with this technique include: contamination from the bellows pump, solvent interferences for very volatile compounds and leakage around ground-glass joints.

Closed-loop stripping with water vapor offers a slight improvement in simplicity as no pump is required but is useful only for compounds of low volatility (e.g., hydrocarbons $>C_{24}$).(107) Materials of lower volatility are largely unrecovered during the stripping process. Tables 6 and 7 give a more complete discussion of the advantage and disadvantages of the technique taken directly from discussions by Melton et al.(117)

Conclusions

Applicability of the Grob method in water analysis is currently being studied. At present very little published research is available.

DIRECT AQUEOUS INJECTION

Principles of the Technique

Analysis of organic compounds in water by direct aqueous injection (DAI) involves analysis in an aqueous medium, by gas-liquid or gas-solid chromatography. Injection volumes, which are typically 1-50 µL, have been used for the determination of volatile organics in various waters. The injection volume depends on the nature and concentration of the compounds of interest, the sample matrix, and the gas chromatographic detector used.

The direct aqueous injection method has been examined for use in detecting and quantifying halogenated compounds in drinking water(63,93,95,122) and for determining organohalides(122,123,124) as well as phenols,(125) amines,(126-128) alcohols,(126) and amides in surface waters and wastewater effluents.(131)

Table 6. DISADVANTAGES OF THE CLOSED LOOP GAS STRIPPING (Grob) METHOD(117)

1. The range of compounds effectively measured by the Grob method is somewhat limited. (1) Highly volatile compounds such as chloromethane, vinyl chloride, methylene chloride and chloroform are poorly recovered and/or covered up by the CS_2 extraction solvent. Therefore, purge and trap(4a) should also be used with the Grob method to provide a comprehensive analysis of purgeable organics. (2) Moderate and highly polar or ionizable organic species are either poorly purged or not recovered at all.

2. Highly contaminated samples, such as industrial effluents, may overload the 1.5 mg activated carbon trap and contaminate the close-loop. A larger capacity 5.0 mg trap, however, is now available.

3. The method requires the development of new laboratory skills (extraction of the trap) before the method can be implemented effectively. This may account for the surprisingly slow acceptance of the Grob method in the United States as compared to Europe. While this procedure can become highly routine in the hands of competent technicians, the method is demanding of careful and consistent manipulations.

4. There is currently no commerical U.S. supplier of the Grob-designed activated carbon filters or filter holders. In addition, there is no worldwide supplier of an integrated, self-contained apparatus. Components must be purchased from a number of suppliers.

5. Grob gas stripping has not been researched comprehensively to optimize analytical conditions and apparatus since Grob and Zurcher [106] standardized the procedure in 1976. It is suggested that the method be optimized to measure purgeable compounds from benzene, toluene and dichlorobenzenes to as high a molecular weight range as is practical.

Table 7. ADVANTAGES OF THE CLOSED LOOP GAS STRIPPING (Grob) METHOD(117)

1. The method is simple, straightforward and rapid. A water sample can go from cold storage to GC/MS injection of the filter extract in about 2.5 h. Sophisticated, electronic "black boxes" are not required. No alteration of a standard capillary GC/MS/DS (equipped with a Grob-type splitless injector) is required. Overall, equipment costs about $1300.
2. The method is ultrasensitive. Good mass spectra can be obtained on most purgeable compounds in the 1 to 10 ng/L range. The GC/MS detection limit of some PCB isomers is 2 ng/L.
3. Blanks are extremely clean. The sample is extracted from the activated carbon filter with only 12 µL of carbon disulfide.
4. Glass or fused silica capillary columns coated with methyl silicone liquid phases can be used with carbon filter extracts for a year or more without developing sample-induced degradation of column performance.
5. The method is relatively trouble-free. The most frequent problem has been contamination of the closed-loop with high molecular weight organics from heavily contaminated water samples. Muffling the glass and metal components of the loop at 450°C for 2 h corrects this problem.
6. On a per-compound-quantified basis, the method is highly cost-effective. Once initiated, sample purging, GC/MS data acquisition and automatic computerized quantification methods proceed virtually unattended. Solvent extraction of the activated carbon trap requires approximately 10 min. Overall, three drinking water samples can be quantified automatically for 215 organics in a 24 h period using 12 person-hours of labor.

Direct aqueous injection implies instrumental analysis by gas chromatography. The selection of specific columns for separating sample components depends on the compound classes under investigation. Paramount in the separation scheme is the removal or retention of water to avoid interference with sample components to be quantified. This is accomplished using a variety of precolumns containing materials such as Ascarite,(131) 10% diglycerol on Chromosorb(123) and Tenax GC®.(132) One commercial instrument allows injection of the aqueous mixture onto a concentrator trap.(57) This trap is subsequently purged with gas to remove water. The retained analytes are desorbed onto a second trap and then introduced onto the chromatography column. As an alternate approach water has been selectively removed by diffusion across a permaselective membrane prior to the sample entering the chromatographic column.(133) Water poses a particular problem when gas chromatography is used in conjunction with mass spectrometry and in at least one instance(126) a vacuum diverter has been used to prevent entry of water into the mass spectrometer.

Chromatographic separation is achieved using a variety of solid supports such as Tenax GC®, Chromosorb 101(95,131) or Porapak Q.(94,95,124,126) Separations involving compounds with amino functional groups have been done on columns containing Carbowax 1500(128) or Pennwalt 223(125) plus 4-7% KOH to minimize peak tailing. Similarly, Apiezon L has been used to determine N-nitrosamines.(129) Methanol and phenol can be determined in wastewater by separation on Tenax GC® deactivated with 85% H_3PO_4 and PPE-20, respectively. In most cases, the columns were operated isothermally at temperatures between 70 and 170°C. Manufacturers' literature for some fused silica capillary columns indicate good performance using the DAI technique. However, some initial work has reported problems with poor peak shape and poor reproducibility for both peak area and retention time for a number of low molecular weight polar compounds.(50)

The lack of sample preconcentration in DAI necessitates that optimal sensitivity be achieved during detection. Flame ionization detectors are useful only when the component concentrations are quite high (~0.1 ppm), as is the case with most energy effluents and wastewaters. Electron capture or Hall electrolytic conductivity detection does possess sufficient sensitivity to detect halogenated hydrocarbons at levels found in drinking waters. Mass spectrometry affords sensitive and selective detection for DAI only when operated in the selected ion monitoring mode. Compatibility of DAI with MS is facile, requiring only that the elution of water from the chromatographic column not coincide with the elution of other sample constituents.

Limits of Detection

The limits of detection for direct aqueous injection depend on the type of detector and the species to be detected. For organohalides in tap water the detection limit using electron capture detection ranges from 0.1-500 ppb, depending upon the degree of chlorination (*i.e.*, more highly chlorinated compounds are detected at lower concentrations).(124,134) Mass spectrometric detection in the selected ion monitoring mode permits detection of 0.1 ppb of organohalides (including vinyl chloride)(122,123) and approximately 50 ppb of aliphatic alcohols, acids and ketones.(126) Amines have been detected by flame ionization at the 10 ppb level.(128) Flame ionization has also been used to detect 500 ppb of methanol.(130)

Compound Types and Recovery Data

Recovery data for the direct aqueous injection technique are presented in Table 8. The scarcity of data reflects a general consensus that recoveries are quantitative, an assumption which is substantiated by available data.

Sample Types

As previously stated, the principal application of direct aqueous injection has been the analysis of haloforms in drinking water.(122,123,134,63,94,95) However, a few successful efforts have applied this technique to surface waters and municipal and industrial wastewaters. Since direct aqueous injection possesses no inherent preconcentration or separation capabilities, the sensitivity and specificity of the technique depend exclusively on the gas chromatographic analysis.(96) Consequently, the analytical protocol is tailored for a particular compound or class of compounds and sample matrix.

Advantages and Disadvantages

The most significant advantages of direct aqueous injection lie in its intrinsic simplicity, minimal expense, and ease of automation. Furthermore, the absence of analytical preparative steps results in low systematic errors and relatively high precision. Typical values for standard deviations range from 1-14%. Coincident with this straightforward analytical scheme is a

Table 8. PERCENT RECOVERIES BY DIRECT AQUEOUS INJECTION

Compound Types	Molecular Weights					
	50	100	150	200	250	300
1. Strong Acids (pKa >6)						
Phosphonic						
Sulfonic						
Carboxylic						
Phenols						
2. Quarterary Nitrogen and Phosphonium Compounds						
3. Amino Acids						
4. Water Soluble Alcohols						
Carbohydrates						
Alcohols	←75-100→					
5. Organometallics						
6. Basic Nitrogen Compound	←75-100→					
7. Weak Acids						
8. Water Insoluble Alcohols						
9. Polar Neutrals						
Aldehydes						
Ketones						
Sulfones						
Nitro Compounds						
Nitriles						
Esters						
10. Nonpolar Neutrals						
Ethers						
Sulfides						
Aliphatic/Aromatic						
Polynuclear Aromatics						
Pesticides and PCBs						

very low potential for sample contamination, which can result only from sampling and gas chromatographic injection techniques. However, this lack of separation and concentration techniques also creates a number of disadvantages. The analysis of drinking waters for haloforms has been found to give higher values by direct aqueous injection than by gas stripping methods (purge and trap).(63,95) This has been attributed to the decomposition of chlorinated nonpurgeable organic compounds (e.g., humic acids) in the injection port of the GC to form chloroform. This artifact seriously undermines the accuracy and applicability of the method for drinking water analysis, as most drinking waters contain both a chlorine residual from the disinfection process and some quantity of humic-like materials. Since the entire matrix is injected into the gas chromatograph, artifact formation varies significantly between sample types.

Accurate analysis for chloroform in drinking water by DAI requires that the chloroform content be assessed both before and after purging the sample with an inert gas with the actual amount determined by difference.(63,95)

Conclusions

Direct aqueous injection has been strongly advocated for detection of halogenated compounds in drinking water because of its simplicity and adaptaability to automated analysis. However, recently reported uncertainties in accuracy have considerably diminshed its popularity. Nevertheless, this method may be satisfactorily applied to water samples in which the interactions between components are known and/or the concentration of the component to be analyzed is such that no preconcentration is required.

STEAM DISTILLATION

Principles of the Technique

Steam distillation is a method of separating chemicals on the basis of vapor pressure differences. At a given temperature, compounds with vapor pressures higher than their environment will volatilize and may be collected by cooling. In applying this technique to trace organic water analysis, two approaches have been used. First, compounds with vapor pressures lower than water or which form azeotropes with water can be concentrated by heating the sample then letting the distillation proceed only until water begins to vaporize and collect in the distillation pot. Theoretically, at this point, all of the volatile compounds have distilled and been collected, thus concentrating them in the water matrix. The second approach is actually a combined distillation/extraction process. Water and organics are vaporized. As the vapors cool, they pass through an organic solvent which extracts the organic contaminants. The spent water is then recycled to the distillation pot. This method not only concentrates volatile and semivolatile compounds, but also separates them from the less volatile organics in the aqueous samples.

Applying the first technique, distillation was performed on a 100 mL sample in a 250 mL round-bottomed flask connected to a 7.75" Vigreux column.(136) During distillation, the vapor pressure at the distilling head was controlled at 100°C and distillation was continued until the first 1.5 mL of distillate was collected. One mL of the distillate was then analyzed via headspace analysis.

Various condensers have been evaluated for aqueous distillations.(135) Concentration factors for polar compounds improved as more efficient condensers were used. The more efficient condenser also gave better concentration factors for large samples.

An azeotropic steam distillation procedure utilized the apparatus shown in Figure 12.(137) As the distillation proceeds, organics with boiling points lower than water or which form azeotropic mixtures with water evaporate from the distillation flask, condense on the condenser and are collected in the distillate chamber. Once the capacity of the chamber is exceeded, distillate empties from the overflow tube. Organics in the distillate then redistill to improve recoveries of test organics in the final distillate with time.

Using an exhaustive steam distillation unit (Figure 13) vaporized organics were concentrated in isooctane or toluene.(138) A 60-minute analysis provided more than 85% recovery for PCBs, p,p'-DDE, mirex and heptachlor epoxide.

An EPA method(7) utilized solvents heavier than water during steam distillation. Volatile organics were collected in methylene chloride in a 50 mL round-bottomed flask. They were dried by Na_2SO_4 and further concentrated in a Kuderna-Danish apparatus to a desired volume for subsequent clean up or analysis.

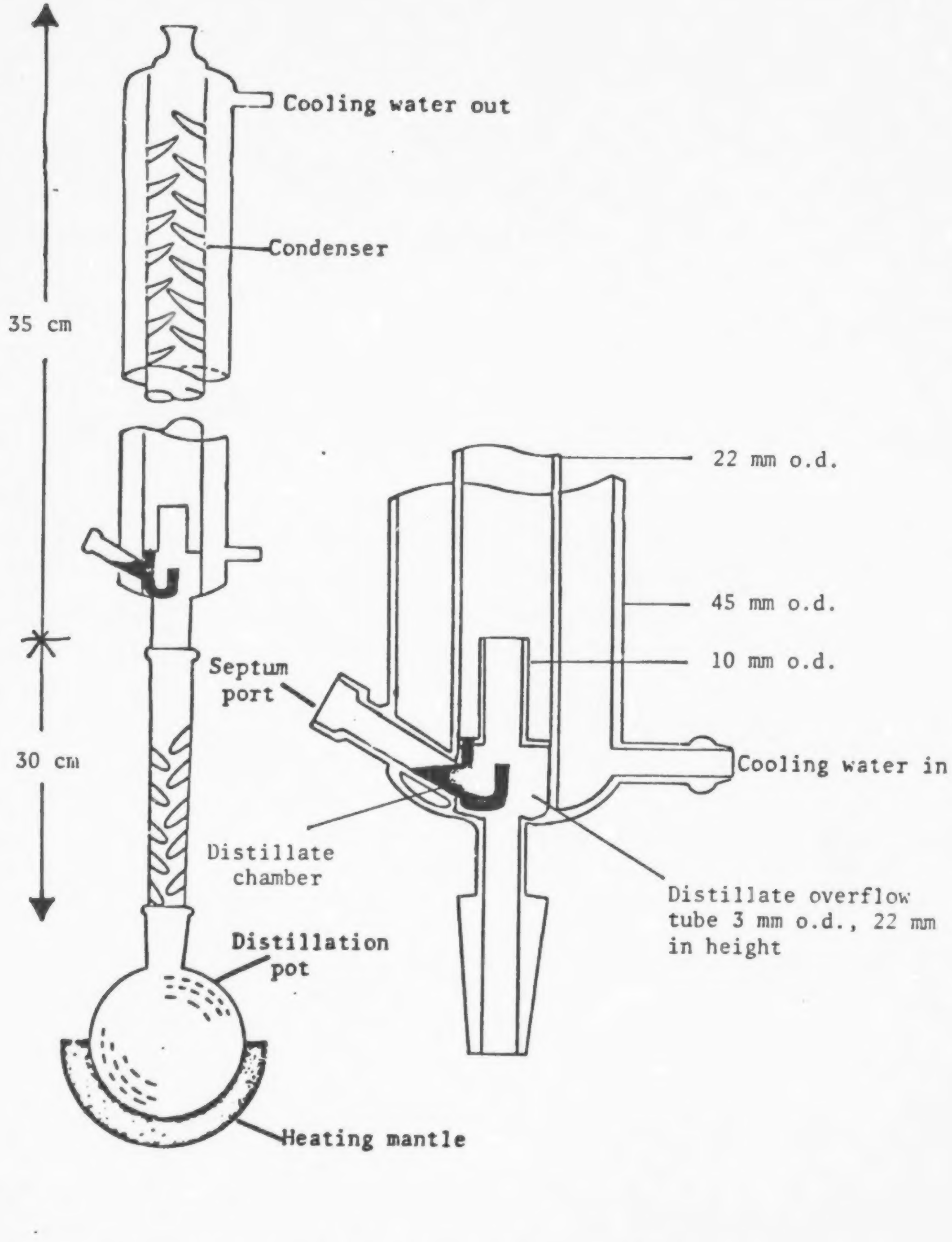

Cooling water out
Condenser
35 cm
30 cm
22 mm o.d.
45 mm o.d.
10 mm o.d.
Septum port
Cooling water in
Distillate chamber
Distillate overflow tube 3 mm o.d., 22 mm in height
Distillation pot
Heating mantle

Figure 12. Modified Peters' apparatus.(135)

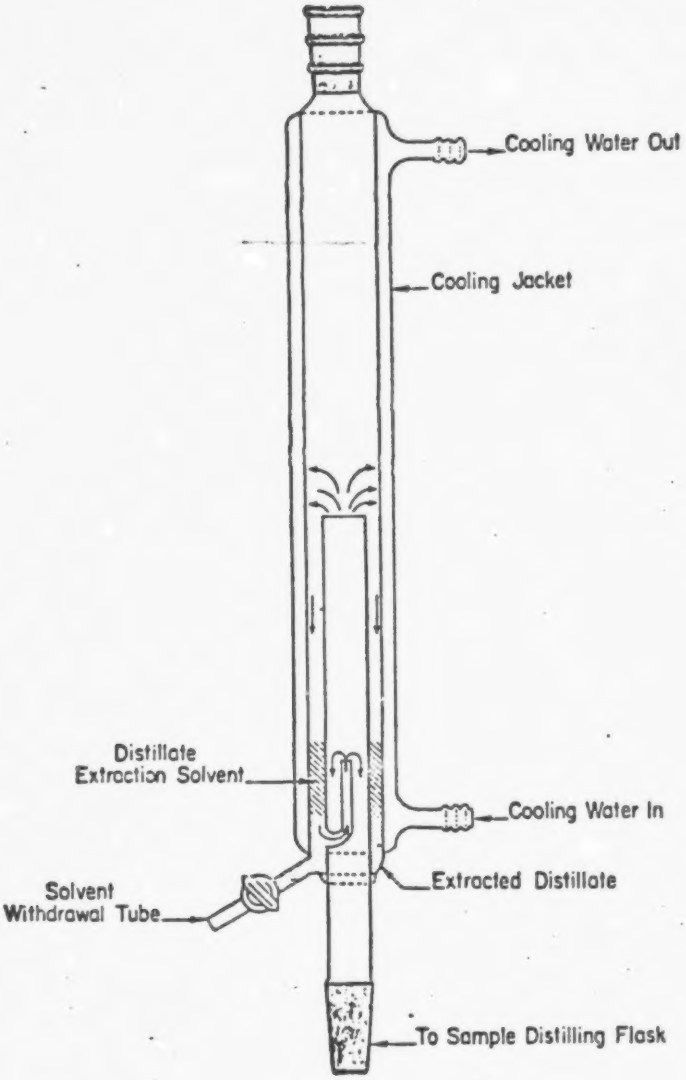

Cooling Water Out
Cooling Jacket
Distillate
Extraction Solvent
Cooling Water In
Extracted Distillate
Solvent
Withdrawal Tube
To Sample Distilling Flask

Figure 13. Exhaustive steam-distillation and solvent-extraction apparatus.

Limits of Detection

Available information on limits of detection and concentration factors for these steam distillation procedures are given in Table 9.

A two-stage aqueous distillation was evaluated to improve concentration factors.(136) Assuming a 90% recovery is achieved in the first 100 mL of distillate from a 1000 mL sample, and 80% is achieved on the first 10 mL of distillate from the 100 mL distillate, the overall recovery will be about 72%, at a concentration factor of 100. Steam distillation has proved particularly useful in enriching highly polar and volatile organic compounds. A recovery of 82% was reported for 2-propanol.

Compound Types and Recovery Data

Procedures which collect aqueous distillates were developed to concentrate polar, water soluble, low molecular weight compounds. Distillation has been recommended as the method of choice for methanol, ethanol, acetone, 2-propanol and methyl ethyl ketone, giving high, reproducible recoveries for these compounds.(3) A list of compounds to which an azeotropic steam distillation technique should be applicable along with boiling point data is included in Table 10.

Extractive distillation concentrates nonpolar, semivolatile compounds. The types of compounds successfully extracted include: various pesticides, trichlorobenzene, naphthalene, chlorophenol, nitrophenol, dimethylphenol, phenol, chloronaphthalene, fluorene, diethyl phthalate, dinitrotoluene, anthracene, fluoranthene, pyrene and ethyl hexyl phthalate. An average recovery rate of over 75% was obtained during experimental evaluation.(21,138)

Recovery data for both procedures are presented in Table 11.

Sample Types

Steam distillation as a concentration technique is applicable to all water types and biomaterials.(108,139-144) Extractive distillation is especially useful for samples with high levels of nonvolatile organics including foods and beverages where it functions as a combined concentration-clean-up procedure.(144) Both methodologies may be used with samples that tend to foam.

Advantages and Disadvantages

Steam distillation/extraction for trace organics analysis is a method of high accuracy and precision. Distillation extraction over isopentane

Table 9. DATA ON CONCENTRATION FACTORS AND LIMITS OF DETECTION (LOD)

		Distillation Dir. Injection	Distillation Headspace	Distillation W/ Solvent	Distillation Salts Na_2SO_4
1.	Initial sample volume	100 mL	100 mL	2500 mL	1000 mL
2.	Final sample volume	not given	1 mL	not given	1.5 - 10 mL
3.	% Recovery	methanol 89% ethanol 93% acetone 87% isopropanol 99%	not given	PCBs *p*,*p*-DDE mirex heptachlor epoxide 85%	not given
4.	LOD (given)	not given	methanol ethanol 8 ppb acetone 2-propanol methyl ethyl ketone 4 ppb	not given	pentanone 5 ppb methanol 40 ppb

Table 10. AZEOTROPIC DATA FOR SEVERAL VOLATILE NONIONIC INTRACTABLES

Compound	Boiling Point, °C	Azeotrope Boiling Point, °C	Weight %
methanol	64	NA[a]	-
ethanol	78	NA	-
1-propanol	97	NA	-
1-butanol	117	93	58
2-butanol	96	NA	-
amyl alcohol	138	96	46
cyclohexanol	161	98	31
hexanol	157	98	33
heptanol	160	99	17
1-octanol	195	99	10
2-chloroethanol	129	98	42
propionaldehyde	48	NA	-
n-butyraldehyde	75	NA	-
crotonaldehyde	104	84	75
furfural	162	NA	-
valeraldehyde	103	NA	-
formaldehyde			
acrolein	52	NA	-
acetone	56	NA	-
methyl ethyl ketone	79	NA	-
cyclopentanone	130	NF	-
cyclohexanone	155	96	45
acetylacetone	141	NF	-
methyl formate	32	NA	-
methyl acetate	57	NA	-
ethyl acetate	77	NA	-
t-butyl acetate	98	NA	-
propyl acetate	102	82	86
allyl acetate	104	83	83
ethyl butyrate	146	NF[b]	-
dimethylfuran	92-94	NA	-

(continued)

Table 10 (cont'd.)

Compound	Boiling Point, °C	Azeotrope Boiling Point, °C	Azeotrope Weight %
tetrahydrofuran	66	NA	-
propionitrile	97	NA	-
acetonitrile	81	NA	-
acrylonitrile	77	NA	-

[a] Since bp is less than 100°C, the effect of azeotrope formation on compound recovery should not be important.

[b] Data not found.

Table 11. PERCENT RECOVERIES BY STEAM DISTILLATION

	Molecular Weights					
Compound Types	50	100	150	200	250	300
1. Strong Acids (pKa >6)						
Phosphonic						
Sulfonic						
Carboxylic					75-100	
Phenols			0-25			
2. Quarterary Nitrogen and Phosphonium Compounds						
3. Amino Acids						
4. Water Soluble Alcohols						
Carbohydrates						
Alcohols	75-100					
5. Organometallics						
6. Basic Nitrogen Compound						
7. Weak Acids-(phenols)		25-50	50-75	75-100		
8. Water Insoluble Alcohols		75-100				
9. Polar Neutrals						
Aldehydes						
Ketones						
Sulfones						
Nitro Compounds			0-25			
Nitriles						
Esters					200-300	
10. Nonpolar Neutrals						
Ethers		75-100			50-75	
Sulfides						
Aliphatic/Aromatic			50-75		75-100	
Polynuclear Aromatics				75-100		
Pesticides and PCBs					75-100	

gave results that agreed very closely with those for direct injection of neat solutions.(145) Efficient concentration of high molecular weight volatile, nonpolar compounds like pesticides can be accomplished easily.(135, 146-148) This method is an effective concentration and cleanup technique wherein inorganic salts and lipids are separated and left as residue in the boiling flask. Organic extracts can be preserved in a small bottle for ease of storage, shipping and subsequent analysis. Degradation of compounds can be avoided by preserving the distillate instead of the original samples. Steam distillation/extraction allows work to be performed on undiluted raw wastes with minimal problems. Emulsions and interferences commonly observed in extraction are minimized or eliminated.

The main problem with steam distillation/extraction is the time involved in the analysis. Depending on the sample type and volume, concentration and extraction may be a matter of hours or days, particularly in the case of drinking water and cleaner samples. The process is time consuming and restrictive as to the number and volume of samples that can be analyzed. Additionally, poor recovery is noted for nitrophenols. They form very strong hydrogen bonds with water and do not steam distill with good efficiency. This is especially true for para-substituted nitrophenols, where less than 6% recovery has been reported.(140)

Simple distillation and azeotropic distillation provide a method for concentrating polar, low molecular weight compounds which cannot be easily extracted. Concentration factors up to 100 fold are possible but often result in reduced recoveries. Azeotropic distillation gives higher recoveries for a broader range of compounds than the simple distillation technique. After concentration, analytes remain in a aqueous solution. If this is the final analytical operation, direct aqueous injection must be used for chromatographic analysis.

For all distillation techniques, high temperature and prolonged heating promote artifact formation.(149) Dirty samples tend to form tarry residues which are difficult to remove from the vessel.

REVERSE OSMOSIS

Principles of the Technique

Reverse osmosis (RO) is a separation process involving the transport of solvent across a suitable membrane against a concentration gradient. If the membrane is truly semipermeable, all solutes originally present in the feed solution will be rejected by the membrane with resultant concentration.(150)

A simple diagram representing the basic elements required in a reverse osmosis sytem is shown in Figure 14. Such a unit consists of a sample reservoir, pressurized feed compartment, semipermeable membrane, and runoff line or collection tank for product water. Actual commercially available or laboratory constructed units will vary in size, membrane type, and pressure source but in principle are identical to the system shown.

Organic rejection is dependent upon solute-membrane interactions. At the present time, only three membrane materials are commonly used for organic separations. The most commonly used membranes are made of cellulose acetate. There seems to be a general correlation between the hydrogen bonding properties of organic solutes and membrane rejection. Dissociated solutes, polyhydric alcohols, and paraffins are best rejected. Unfortunately, cellulose acetate membranes hydrolyze under highly acidic or basic conditions generally restricting their operational pH range and rejection potential.(151) The NS-1 membranes are condensation polymers of amide and isocyanate. These membranes show higher organic rejection than cellulose acetate, with exclusion based primarily on solute size rather than functional group.(152) Good solute rejection and a wide operational pH range are the major advantages of this membrane type. Unfortunately, these membranes degrade when exposed to high chloride ion concentrations (1 ppm or greater), thereby limiting their practical application. Finally, polyamides are the third type of commonly used membranes. They are similar to the NS-1 membranes showing parallel behavior in terms of both rejection properties and chloride sensitivity.*

Although none of these membranes are ideal, it should be possible to design an RO unit using a combination of membranes to give the desired concentration properties. For example, cellulose acetate could be used to remove large charged organics, as well as chloride ions at a neutral pH. Then a second membrane, either polyamide or NS-1, could be placed in series, to concentrate weak acids and bases after pH adjustment.(153)

Concentration Factors

Concentration factors for reverse osmosis obviously depend upon the size of the starting sample in relation to the size of the final solutions. For a large sample input with multiple runs through the membrane, this

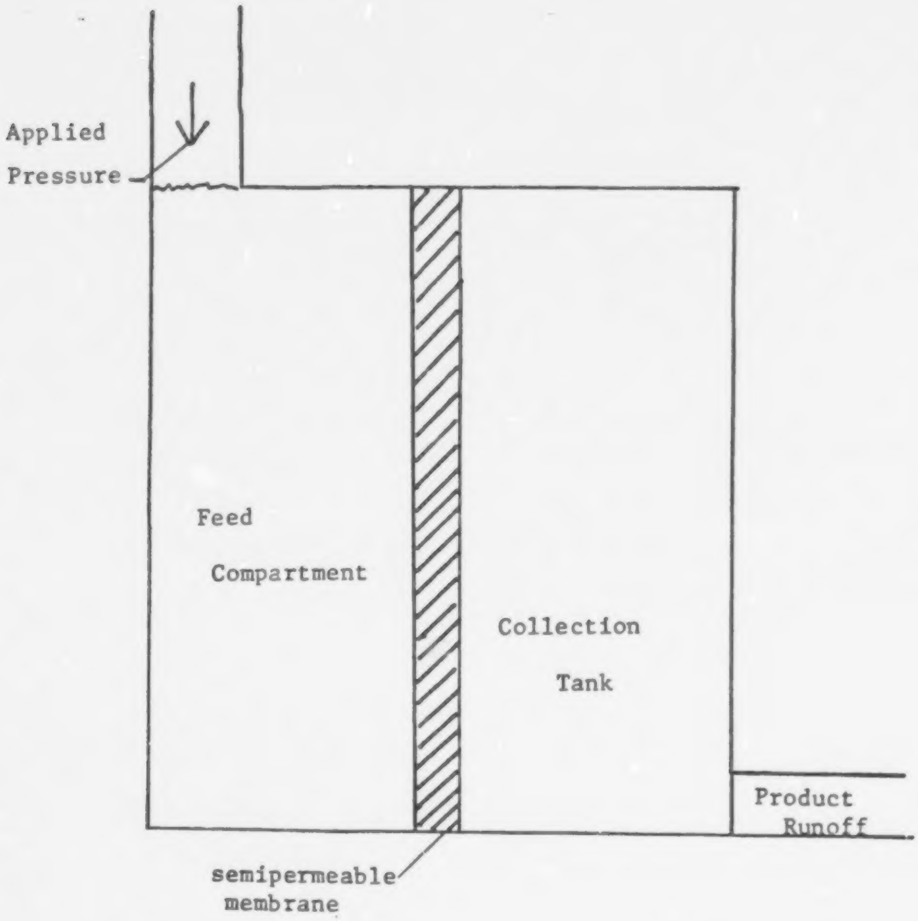

Applied
Pressure
Feed
Compartment
Collection
Tank
Product
Runoff
semipermeable
membrane

Figure 14. Reverse osmosis unit.

factor could be a thousandfold or greater. The sample, once concentrated, is still in an aqueous matrix which must be removed prior to subsequent analysis.(154) If very polar water soluble compounds are to be analyzed, freeze-drying, followed by chemical derivatization and GC/MS, could be used.

Compound Types and Recovery Data

Membrane rejection depends upon several basic mechanisms:(134,155,156) size exclusion;(157-160) electrostatic repulsion;(161-163) and solute membrane solubility.(151,164-168) Tables 12 and 13 give rejection values for the range of compounds which have been studied. In this case, rejection (R) is defined as:

$$R = 1 - C_p/C_f$$ (169)

where C_f and C_p are concentrations of solute in the feed and product water respectively. If an organic solute preferentially permeates the membrane compared to water then the term C_p/C_f is greater than 1 and R is negative. Rejection values for all three membrane types have been reported, and are included as such in the Tables.

Sample Types

Reverse osmosis techniques should be applicable to all water types with two restrictions in mind. High salt concentrations in feed water may cause problems with precipitation and membrane fouling. Also, various membranes are sensitive to hydrogen, hydroxy, and chloride ions, thereby limiting their use in certain waters. Experimentally, reverse osmosis techniques have been applied to drinking, surface, and industrial wastewaters for organic concentration prior to analysis.(151,152,154,158,159,164) To date, reverse osmosis has not been applied to energy effluents but high contaminant levels in these samples generally eliminate the need for concentration procedures.

Advantages and Disadvantages

The major advantage of reverse osmosis is its ability to concentrate organics from very large water samples. In contrast to sorbent columns which also provide this capacity, reverse osmosis concentrates organics regardless of their physical state (particulate, complex, colloidal, or dissolved). Reverse osmosis does not involve a phase change and therefore is not as discriminatory against hydrophilic polar organics. It is a low-

Table 12. PERCENT REJECTION BY REVERSE OSMOSIS (CELLULOSE ACETATE)

Compound Types	Molecular Weights					
	50	100	150	200	250	300
1. Strong Acids (pKa >6)						
Phosphonic						
Sulfonic						
Carboxylic		75-100	25-50			
Phenols						
2. Quarterary Nitrogen and Phosphonium Compounds						
3. Amino Acids						
4. Water Soluble Alcohols						
Carbohydrates				75-100	75-100	75-100
Alcohols	0-25					
5. Organometallics						
6. Basic Nitrogen Compound		0-25	75-100	50-75		
7. Weak Acids-(phenols)		0-25	0-25	0-25		
8. Water Insoluble Alcohols		25-50	25-50	75-100	75-100	
9. Polar Neutrals						
Aldehydes	25-50	25-50				
Ketones						
Sulfones						
Nitro Compounds				75-100		
Nitriles						
Esters		0-25	0-25			
10. Nonpolar Neutrals						
Ethers		25-50	25-50			
Sulfides				75-100	75-100	75-100
Aliphatic/Aromatic		50-75	75-100	75-100	75-100	
Polynuclear Aromatics						
Pesticides and PCBs						

Table 13. PERCENT REJECTION BY REVERSE OSMOSIS (NS1, POLYAMIDE)

Compound Types	Molecular Weights					
	50	100	150	200	250	300
1. Strong Acids (pKa >6)						
Phosphonic						
Sulfonic						
Carboxylic	←50-75→	←——	——75-100→			
Phenols						
2. Quarterary Nitrogen and Phosphonium Compounds						
3. Amino Acids						
4. Water Soluble Alcohols						
Carbohydrates						
Alcohols						
5. Organometallics						
6. Basic Nitrogen Compound		←75-100→				
7. Weak Acids-(phenols)		←——	——50-75→			
8. Water Insoluble Alcohols		←——	——75-100→			
9. Polar Neutrals						
Aldehydes	←25-50→					
Ketones		←——	——75-100→			
Sulfones						
Nitro Compounds	←50-75→					
Nitriles						
Esters	←25-50→	←——	——75-100→			
10. Nonpolar Neutrals						
Ethers			←——	——75-100→		
Sulfides						
Aliphatic/Aromatic			←75-100→			
Polynuclear Aromatics						
Pesticides and PCBs						

energy rapid process, especially when compared to other aqueous phase concentration techniques (freeze-drying or flash evaporation). Since a phase change is not involved and concentrations are performed at ambient temperatures, the possibility of side reactions and artifact formation is minimized.

Most of the disadvantages of reverse osmosis result from the fact that it has been used primarily as a commercial technique for removing inorganic ions during water treatment. Lab scale RO units with membranes appropriate for organic concentration and analysis are not available. Commercially available units have large dead volumes in the feed compartment (8 gallons or greater), which means that very large samples must be processed in order to achieve adequate concentration. Commercially available membranes are not designed specifically for organic rejection and therefore do not always have the desired characteristics. They usually contain high concentrations of plasticizers causing severe contamination problems. Membrane-organic interaction can cause problems for qualitative analysis. For example, high membrane absorption for various pesticides and other organics has been reported.(165) Likewise, the rejection properties of cellulose acetate membranes can change during operation depending upon the concentration and type of aqueous solute species present.(166) Certain membranes are pH limited or sensitive to high chloride ion concentrations which may severely restrict their applicability to many water types. Finally, since very little work has been done using reverse osmosis as a concentration step for organic environmental analysis, the technique is not fully characterized nor have its utilities and drawbacks been fully defined.

Conclusions

Actual analysis using reverse osmosis as a concentration technique for organics in environmental water samples has been limited. The most extensively used system is a mobile unit designed for concentrating large quantities of organics from surface and drinking waters.(151,153) Toxicity testing and specific qualitative analysis on sample extracts have been performed by independent laboratories. Considerably more research must be done to develop the capabilities of reverse osmosis for organic concentration. When problems of membrane selectivity, unit design, and membrane adsorption are overcome, then this could be a preferred method for isolating both ionic and hydrophobic organics from environmental water samples.

FREEZE-DRYING/LYOPHILIZATION

Principles of the Technique

The freeze-drying or lyophilization process is essentially a low temperature, low pressure distillation of water which sublimes from the surface of ice and condenses in a cold trap. It is a method commonly used for drying biological tissues and desalination of seawater. The sample is frozen at 40°C, and a vacuum of approximately 0.1 torr is applied to evacuate the system and allow for the sublimation of water, leaving a residue of non-water components consisting of inorganic salts and nonvolatile organic matter. The inorganic salts can be precipitated, and fractions of interest analyzed by high resolution liquid chromatography or gas chromatography and mass spectrometry. The dehydration capacity can be improved by adding 3-10% ferric chloride or 0.3-0.7% cationic electrolytes.(170)

In the determination of organophosphorus compounds,(171-173) water was filtered prior to lyophilization using a 0.45 μ membrane. The concentrate was then diluted with 0.05 M ammonium carbonate and a cation exchanger was used to convert the calcium and magnesium ions to sodium ions to minimize their interference with the resolution of dissolved organic phosphorus compounds. Recoverable organic phosphorus compounds had a molecular weight of more than 50,000.

Multistep lyophilizations have also been employed.(174,175) For example, in one study water samples were filtered, then vacuum-distilled to reach a 5- to 100-fold concentration. Precipitated solids were treated with acetic acid to destroy the carbonates and redissolve adsorbed organics. The concentrate was then centrifuged to remove inorganic salts. The acidified supernate was lyophilized and the residue was separated using high resolution anion exchange chromatography. The eluate was again lyophilized, redissolved in methanol, and analyzed by GC/MS. No quantitation was performed.

Limits of Detection and Concentration Factors

Lyophilizers may be as large as 100 L capacity. Theoretically lyophilization should permit adjustment of the final volume to give any desired concentration factor. However, the time required for this operation is often prohibitive.

Considering the capacity of a lyophilizer to be 3 L, performance time may easily exceed 70 hours, depending on the sample type. If the lower limit of detection for high resolution liquid chromatography with a UV photometer is assumed to be 100 μg/L, then a concentration factor of 100 would be necessary to achieve a 1 ppb detection limit. Drying times of 2 to 3 days for 100 g of ice at a vacuum of 10 to 50 millitorr has been reported.(176) Mass spectrometer sensitivity is somewhat lower than HLPC/UV detection, but even here high concentration factors are needed.

For direct lyophilization in hard waters, only a limited degree of concentration (10-20x) can be obtained due to the binding effects of inorganic salts to water. Insufficient dehydration when water was present in the adsorbed and crystal form has been reported.(177)

Compound Types and Recovery Data

Freeze drying is most suited to water soluble, non-volatile compounds or labile biological and other heat-sensitive materials. Among the compounds concentrated using this technique were: fatty acids, carbohydrates, amino acids, nucleotides, metabolites, urea, mannitol, xylitol, aliphatic acids, pyridines and organophosphates. Aqueous solutions of parathion, malathion and dichlorvos were lyophilized prior to quantitative analysis.(178) Low molecular weight carboxylic acids and sulfonic acids were freeze dried after conversion to nonvolatile salts.(179)

In the process of concentration, most volatile organics are lost, particularly when they are not bound to any dissolved solids. No recoveries for diethyl ketone at 7 ppm, iso-amyl acetate at 4 ppm and iso-amyl alcohol at 80 ppm were reported.(180) A maximum recovery of 11% was obtained when 1% pectin or protein was added to the water. In recovery studies, problems have been encountered with radiolabeled compounds. Tritium exchanges frequently occur. Quantitative recoveries of amino acids have been reported. For environmental samples reported recoveries of total organic carbon were over 90%, but no recoveries of specific compounds were given.

Sample Types

Lyophilization is applicable to all water types and biological materials. However, as already mentioned, very hard or alkaline water may limit effective concentration.(177)

Advantages and Disadvantages

Freeze drying is a preferred process for labile biologicals and other heat-sensitive materials. Minimum treatment is applied to the samples and they are preserved in their original forms. The effects of heat, oxidation and decomposition are eliminated. There is no problem with artifact formation. Since organics are concentrated in their aqueous phase, matrix effects are minimized. However, lyophilization is a very time consuming, high energy process when large sample volumes are involved. Problems associated with recoveries of volatile compounds have also limited its use.

Conclusions

Lyophilization is frequently used to dehydrate small biological samples. In contrast, its use in environmental analyses has been limited. Oak Ridge National Laboratory(174,175) uses lyophilization for the routine analysis of organic compounds in environmental water samples, but this is done only for the purposes of identification. No quantitation has been performed.

ION EXCHANGE

Principles of the Technique

Ion exchange is an adsorption process involving the displacement of resin ions by solute ions of similar charge. Functional groups on the surface of a solid sorbent provide sites for electrostatic exchange.(181) Theoretically, ion exchange processes should remove any ionic species from an aqueous solution making ion exchange a valuable technique for concentrating charged polar organics or removing inorganic ion interferences from environmental water samples.

Generally, an ion exchange resin consists of a hydrocarbon backbone with soluble ionic functional groups attached. The concentration of ionic groups within the resin determines exchange capacity, while the chemical nature of the groups effects both ion exchange equilibrium and general ion selectivity.(182) Table 14 outlines types of ion exchangers, their chemical nature, and general ion affinity. Table 15 lists some specific ion exchange materials and summarizes their properties.

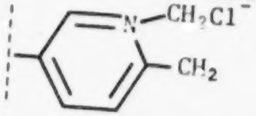
The extent of cross-linking within the hydrocarbon backbone determines the internal pore structure of the resins. Because ions must diffuse into and out of the resin matrix for exchange to occur, ions larger than a given size may be excluded from adsorption. This may be a limiting factor, especially for large organic molecules.

During concentration, an aqueous solution is passed through the resin column, allowing exchange to take place. Adsorbed ions are then eluted

Table 14. ION EXCHANGERS

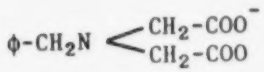
Type	Class	Functional Groups	Chemical Affinity	Counter Ions
Cation	Strongly acidic	$R\text{-}SO_3^{(-)}$	All (+) ions, organic ions	H^+, Na^+
Cation	Weakly acidic	$R\text{-}CO_2^{(-)}$	Strongly hydrolyzed cations, usually inorganic	H^+. Na^+
Anion	Strongly basic	$R\text{-}R'_3N^+$	All (-) ions, organic ions	OH^-, Cl^-
Anion	Weakly basic	$R\text{-}NH_3^+$	Strongly hydrolyzed anions, usually inorganic	OH^-, Cl^-

Table 15. RESIN PROPERTIES SUMMARY(189)

Resin Type	Active Group	Selectivity	Order of Ionic Selectivity
AG 1 Strongly Basic Anion Exchanger	$\phi\text{-}CH_2N^+(CH_3)_3$	$Cl^-/OH^- \cong 25$	$I>\text{phenolate}>HSO_4ClO_3>NO_3>Br>CN>HSO_3>NO_2>Cl>HCO_3>IO_3>H_2>COO>Ac>OH>F$
AG 2 Strongly Basic Anion Exchanger	$\phi\text{-}CH_2N^+(CH_3)_2$ C_2H_4OH	$Cl^-/OH^- \cong 1.5$	$\text{phenolate}>I>HSO_4>ClO_3>NO_3>Br>CN>HSO_3>NO_2>Cl>OH>IO_3>H_2COO>Ac>F$
Bio-Rex 9 Strongly Basic Anion Exchanger		not given	not given
AG 21K Strongly Basic Anion Exchanger	$\phi\text{-}CH_2N^+(CH_3)_3$	$Cl^-/OH^- \cong 15$	$I>NO_3>Br>Cl>Ac>OH>F$
Bio-Rex 5 Intermediate Base Anion Exchanger	$R\text{-}N^+(CH_3)_2$ C_2H_4OH & $R\text{-}N^+(CH^3)^2$	not given	not given
AG 3-X4A Weakly Basic Anion Exchanger	$\phi\text{-}CH_2H^+(R)_2Cl^-$	not given	$\phi SO_3H>HCit>CrO_3>H_2SO_4>\text{tartaric}>\text{oxalic}>H_3PO_4>H_3AsO_4>HNO_3>HI>HBr>HCl>HF>HCOO>HAc>H_2CO_3$

(continued)

Table 15 (cont'd.)

Resin Type	Active Group	Selectivity	Order of Ionic Selectivity
AG 11A8 Strongly Basic Anion plus Weakly Acidic Cation (Zwitterion)	$\phi\text{-CH}_2\text{N}^+(\text{CH}_3)_3$ & $\text{R-CH}_2\text{-COO}$	not given	not given
Chelex 100 Weakly Acid Cation Chelating Resin	 $\phi\text{-CH}_2\text{N} < \begin{matrix}\text{CH}_2\text{-COO}^- \\ \text{CH}_2\text{-COO}\end{matrix}$	$\text{Cu}^{++}/\text{Na} \gg 100$	H>Li>Na>K Cu>Pb>Fe>Al>Cr>Ni> Zn>Ag>Co>Cd>Fe>mn> Ba>Ca>Na
Bio-Rex 70 Weakly Acidic Carboxylic Cation Exchanger	R-COO^-	not given	H≫Ag>K>Na>Li H≫Fe>Ba>Sr>Ca>Mg
AG 50 or 50W Strongly Acidic Cation Exchanger	ϕSO_3^-	$\text{Na}^+/\text{H}^+ \cong 1.2$	Ag>Rb>Cs>K>NH_4>Na> H>Li Zn>Cu>Ni>Co

either by neutralizing the charge on the solute or by rinsing the column with a highly concentrated solution of counterions. Eluting solutions for organic acids have included HCl in methanol,(183,184) HCl in diethyl ether,(199) and $NaHSO_4$ in a mixture of water/acetone or acetonitrile/acetone.(184,185,186) Organic bases have been eluted with KOH in acetonitrile.(184)

In highly saline solutions, resin capacity may be quickly saturated with inorganic ions to give low and variable recoveries for the organics of interest.(187) Ligand exchange, a variant of ion exchange, often circumvents this problem. A version of the technique uses Cu^{+2} saturated ion exchange columns. In principle, copper ions form very stable chelates with molecules such as ammonia, amines, and amino acids but are unreactive toward inorganic salts.(188) Under these conditions selective anion concentration should be achieved. Recoveries greater than 90% have been realized for amino acids.(190,191) However, experiments with nitrilotriacetic acid (NTA) gave very poor results.(192)

Concentration Factors

Since most ion exchange procedures utilize column techniques, sample volumes are restricted only by ionic strength of the sample. Actual concentration factors depend upon sample size, eluate volume, ion exchange capacity, and total ion concentration. Sample concentrates from ion exchange are usually dissolved in aqueous or polar solvents which may require further concentration and fractionation prior to analysis. Final concentration factors and limits of detection depend upon the subsequent procedures employed.

Compound Types and Recovery Data

Ion exchange resins are capable of concentrating any ionic species from an aqueous matrix. However, since this involves sorption processes, preferential accumulation will occur. Ionic selectivities are greatest for low molecular weight organics, compounds containing multiply-charged functional groups, and ions capable of specific interaction(193) (i.e., amino acid complexation on ligand exchange resins).

Cation exchange resins have been used for years to concentrate amino acids from natural waters.(194,195) These resins have also been applied to the accumulation of synthetic chelating agents such as NTA(192,196,197) and EDTA.(198) Methodologies for concentrating phenols(147) and phenoxy acids(147) have been developed using anion exchange resins. Phosphoric acids(198) and dicarboxylic acids have also been analyzed using anion exchange resins. For most applications, pH adjustment has been used to promote organic dissociation. Once the ionic species is obtained, high recoveries are usually achieved. Recently, XAD resins have been derivatized with polar functional groups effectively converting them to ion exchangers. Quantitative recoveries for benzenesulfonic acid and organic phosphates have been achieved. These converted resin materials have also been used for the simultaneous concentration of neutral, hydrophobic compounds.(199)

An extensive fractionation scheme for analysis of aqueous environmental samples has been developed using XAD resins in conjunction with ion exchange resins.(193,200) Neutral lipophilic compounds are adsorbed by the resins. Low molecular weight ($\leq$5 carbon atoms) and polyfunctional acids are concentrated on anion exchange columns, while the accumulation of basic compounds (aliphatic amines, pyridine, and amino acids) is effected using cation exchangers. Quantitative recoveries for citric acid and ethylene diamine were demonstrated. Originally, samples were acidified using HCl, but this procedure was later modified by introducing hydrogen(193) ions from cation exchange resin in its H+ form. This approach introduced additional ions which would later require removal.

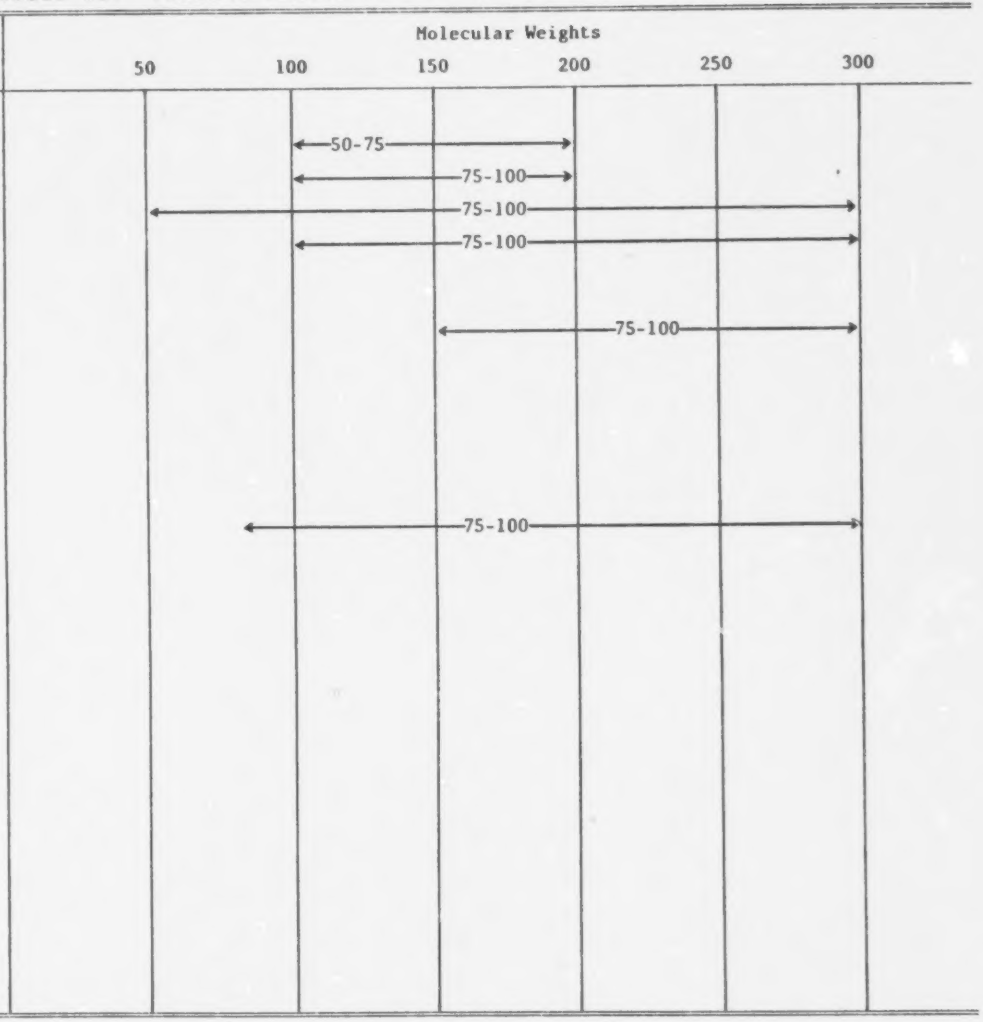
Weak cation exchange columns have been used to remove ammonia and alkalinity from oil shale retort waters.(201) These resins should remove only strongly hydrolyzed cations without affecting the less basic organic ions. Similarly, a Donnan cation exchanger has been used to remove hardness from surface and drinking water prior to reverse osmosis.(154) Commercial water demineralization processes have been developed using ion exchange.(181) Both cation and anion resins are utilized in their hydrogen and hydroxide forms, respectively. Ions released from the resins are simply hydrogen and hydroxide ions which will contribute nothing to the dissolved solids concentration of the water.(151)

A summary of recovery data for organic compounds is given in Table 16.

Sample Types

Concentration using ion exchange resins has been reported for drinking and surface waters,(193-202) municipal,(199,202,203) industrial,(94) and energy effluents.(186) Problems within each of these matrices depend upon the identity and concentration of interfering ionic and organic species. Any water with high levels of inorganic ions including sea water, some waste

Table 16. PERCENT RECOVERIES BY ION EXCHANGE



Compound Types	Molecular Weights
1. Strong Acids (pKa >6)	
Phosphonic	50-75
Sulfonic	75-100
Carboxylic	75-100
Phenols	75-100
2. Quarterary Nitrogen and Phosphonium Compounds	
3. Amino Acids	75-100
4. Water Soluble Alcohols	
Carbohydrates	
Alcohols	
5. Organometallics	
6. Basic Nitrogen Compound	
7. Weak Acids-(phenols)	75-100
8. Water Insoluble Alcohols	
9. Polar Neutrals	
Aldehydes	
Ketones	
Sulfones	
Nitro Compounds	
Nitriles	
Esters	
10. Nonpolar Neutrals	
Ethers	
Sulfides	
Aliphatic/Aromatic	
Polynuclear Aromatics	
Pesticides and PCBs	

effluents, and very hard or alkaline waters will prematurely exhaust resin capacity or cause preferential exchange to desorb organics. Metals present in solution may cause chelation reactions with ionic organics, thereby preventing resin sorption. For example, low recoveries for NTA have been reported at neutral and alkaline pH's when copper is present in the solution.(192) Municipal waste effluents with high humic acid content have blocked resin columns.(202) Further, interactions between organics and humic acids or other high molecular weight materials may cause lower resin concentration factors. Ion exchange resins are also used to concentrate both acids and bases from biological samples.(204-207)

Advantages and Disadvantages

The major advantage of ion exchange resins is their ability to concentrate ionic organics. This is the only technique to provide both high concentration factors and good recoveries for amino acids, amines, and low molecular weight and polycarboxylic acids. Because most resin exchanges are performed using accumulator columns, it is possible to process large volumes of water, thereby providing very high concentration capacities. Ion exchange is a selective process which will not adsorb all organics; therefore, the technique can be used to provide sample fractionation as well as concentration during processing. The scheme devised at USGS using resin and ion exchange columns is an excellent example of this approach.(193,200) Sample concentrates of sewage effluents using ion exchange resins showed fewer GC interferences than those obtained from either solvent extraction or steam distillation techniques.(147) Finally, weak acid and basic resins can be used to remove interfering inorganic ions. Removal of low solubility salts, metals, ammonia, and carbonates has been effected using this technique.

Many of the disadvantages of ion exchange are those inherent to any sorbent technique. First, resins adsorb only dissolved species. Organics adsorbed on particulate matter or associated with high molecular weight humic or fulvic acids will not be concentrated. These types of analyses are particularly sensitive to matrix effects. Second, resin accumulation often does not result from a single type of reaction. Although electrostatic attractions are the major driving force for accumulation, all resins contain a hydrocarbon backbone which can lead to hydrophobic adsorption. For example, low accumulations of neutral organics on exchange resin during phenol analysis have been reported.(208) Finally, unless scrupulously cleaned, resins may be a source of sample contamination: high levels of organic interference measured as TOC have been reported during recovery studies with citric acid on anion exchange resins.(200)

Conclusions

Ion exchange is an established technique for removing or concentrating ionic species from water, but its use in environmental analysis has been limited. For work specific to ionic and hydrophobic chemicals, ion exchange should provide an efficient, reliable, well-characterized method for solute concentration.

SORBENT COLUMNS

Principles of the Technique

The use of sorbent columns in the determination of organic compounds in water is an application of liquid-solid chromatographic techniques (LSC). Compounds are isolated from the aqueous matrix by adsorption onto a solid phase which is composed of small particles of commercially available materials including carbons, resins, and foams.

During concentration, analytes should be adsorbed by the resin material while water passes through the column. However, the capacity of the sorbent for the analyte is finite and, eventually, the solute will no longer be retained by the column. At low analyte concentrations (less than 100 ppm) volumetric capacity determines breakthrough characteristics.(209) Under these conditions, analyte partitions between the sorbent material and the sample matrix exactly as in a chromatographic process, and analyte breakthrough is related to sorbent affinity. This process causes breakthrough to occur well below the weight capacity limit and should be concentration independent as has been verified over the range of 50 ppb to 50 ppm for nondissociated solutes.(210)

Sorbed analytes are eluted from the solid phase with a solvent or solvent mixture for which they have a high affinity. Solvents such as methanol,(211-214) ethanol,(215) acetone,(216-218) diethyl ether,(216-225) acetonitrile,(226) chloroform,(217,218) and methylene chloride(211) have been used either alone or as solvent mixtures. Water at an alkaline pH(210) or weak organic bases(227) have been used to recover organic acids from resin columns. Alternately, thermal desorption has been used to recover analytes from a number of sorbent materials. This technique is most commonly applied to Tenax GC®, but has also been reported for XAD resins.(228-230)

During concentration, the solid phase particles are packed in a column and the water is passed through the column, either at the collection site or in the laboratory. Because of the chromatographic effect columns of approximately 10 grams have been used. A minicolumn procedure for concentrating organics with a high affinity for the resin material has also been reported using XAD-4 or Spherocarb.(231) The sorbed materials were eluted with 50 to 100 μL of organic solvent.

Several investigators have evaluated the effect of sample flow rate on analyte recovery. Experiments with XAD resins and anion exchange resins have demonstrated that linear or face velocity through the resin bed limits the efficiency of mass transfer.(232,233) A flow rate of 2 mL/minute gave maximum adsorption of phenol on XAD-2 resin.(234) Nonpolar materials can be adsorbed at faster flow rates.(235)

Resins must be cleaned before use in a sampling environment to ensure sufficiently low blank values. Sequential Soxhlet extraction in three solvents (methanol, acetonitrile, diethyl ether) is reported to give the best results.(210) The low temperature and wet environment apparently minimize disruption of the particles and subsequent exposure of new contaminated inner surfaces. This sequential extraction method was preferred over both vacuum degassing at 225°C and thermal desorption in a 200°C inert gas stream. Evidently, storage of the cleaned resins is also critical. High blank values of naphthalene, ethylbenzene and benzoic acid were attributed to improper storage. The contaminants are allegedly trapped inside the resin bead during formation and if the resin is allowed to dry out these compounds are released from the interior. Storage under methanol is therefore generally recommended.

Concentration Factors

This sample preparation technique using sorbent columns provides a concentration factor sufficiently great for detection of individual substances at the part-per-billion (ppb) level. Precise concentration factors depend on the volume of sample passed through the column, the volume of eluting solvent used, and the extent to which the eluate is concentrated. An eluting solvent can be chosen which will result in highly efficient recoveries of the adsorbed materials and which will be compatible with gas chromatographic (GC) or gas chromatographic/mass spectrometric (GC/MS) analysis.

Compound Types and Recovery Data

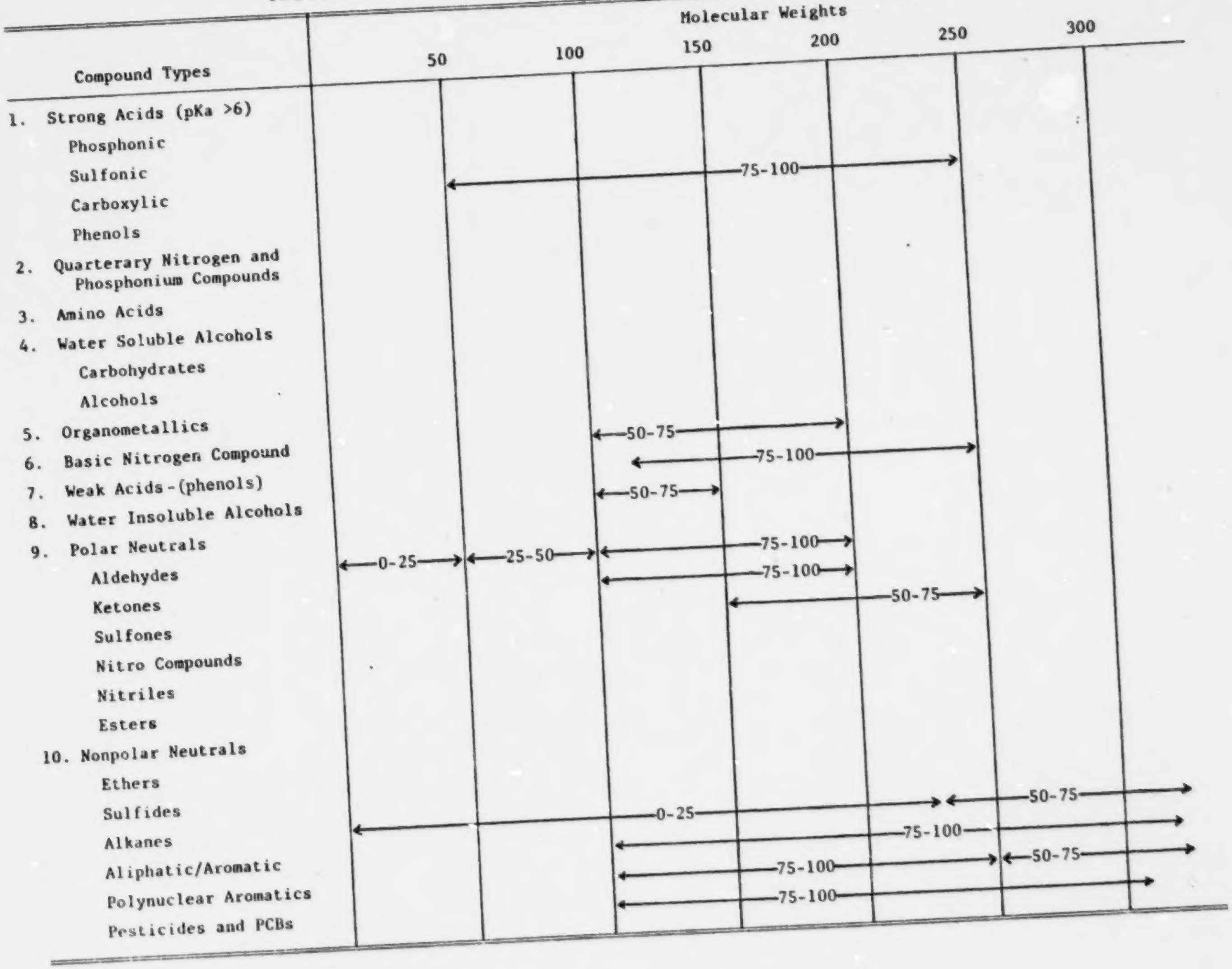
Table 17 shows the applicability of sorbent columns to water analysis. In this table, recoveries for various classes of compounds are given as a function of molecular weight.

Several sorbent materials are being investigated for separating organic constituents from water. The utility of charcoal or carbon as a purifying agent has long been known; in the early 1960's a procedure for filtering water through granulated activated carbon was incorporated into a number of municipal water treatment facilities. Activated carbon has been used to isolate chlorinated insecticides from surface waters(236) and N-nitroso compounds from drinking water(237) using chloroform as the eluting solvent. This sorbent has also been used in a procedure to determine tetrahydrofuran, acetone, several dioxins and higher alcohols in wastewater, drinking water, and ground water. In general, activated carbon is suitable for adsorption of middle and higher molecular weight organic compounds.(238,239) However, it is difficult to elute the adsorbed substances completely and there is evidence that chemical changes can occur on the surfaces of the carbon particles.(240)

Amberlite XAD resins have been widely used in sorbent columns. These macroreticular resins are hard, insoluble beads of crosslinked porous polymer. Their surface polarities range from nonpolar to very highly polar and a variety of surface areas, porosities, and pore size distributions is represented. The surface properties of four of these adsorbents have been summarized.(221)

XAD-2 has been used in the determination of nonpolar organics in water. Using this resin, good recoveries have been obtained in the determination of higher alcohols, ketones, esters, and phenolic compounds in drinking water,(241) aliphatics, aromatics, alkylbenzenes and naphthalenes in seawater,(242) chlorinated pesticides in river water, ground water, industrial wastes, and drinking water,(224,226,243,244) a variety of nonpolar compounds in river water and halogenated hydrocarbons in drinking water.(245) A number of other studies involving XAD-2 (223,246-248) have been aimed at isolating

Table 17. PERCENT RECOVERIES WITH SORBENT COLUMNS



moderate to high molecular weight nonpolar organic compounds from a variety of aqueous samples. There have been reports that XAD-2 contributes significant background contamination during analysis and that breakthrough volume is low.

Amberlite XAD-4 is another resin which has been used in sorbent columns. Phenoxyacetic acids in distilled and river water,(249) chlorinated insecticides and polychlorinated biphenyls in drinking water(221) have been reported.

XAD-7 and XAD-8 are acrylic ester resins. In comparison to the other XAD resins they gave the most efficient adsorption and elution of fulvic acid.(250)

A few other materials have been investigated for their ability to remove organic compounds from water. These include polyamide resin beads which have been used to isolate acid and base/neutral extractable compounds from groundwater,(251) polyurethane foams which have been used to isolate chlorinated insecticides in natural waters,(219,252) Chromosorb W coated with Carbowax 4000 monostearate and undecane to remove chlorinated pesticides and PCBs from a number of water types,(220) Tenax GC® mixed with 60-80 mesh glass beads to analyze for a variety of organics in tap and surface waters,(253) Chromosorb 102 which was used to isolate substituted phenols spiked into distilled water,(254) and surface-bonded $[C_{18}H_{37}S_1O_3/2]_n$ on Chromosorb G to remove a number of chlorinated hydrocarbons from distilled water.(255) Aliphatic and aromatic hydrocarbons in seawater(256) have been determined using this material. These sorbent materials have not received much attention due to a lack of adsorptive capacity or to the irreversible character of their adsorptive processes. XAD-4 has been found to be superior to XAD-2 in terms of efficiency of adsorption and subsequent desorption of nonpolar organic compounds. Large volumes of water can be processed using XAD-4 sorbent columns and problems with breakthrough and contamination are minimal.(210)

Other macroreticular resins which have been used for water analysis are XAD-7 and XAD-8. These resin materials have been used to isolate the neutral and the more polar hydrophilic organics from aqueous samples. Using these sorbents good recoveries have been obtained for the determination of halogenated phenols in surface water,(257) phenols and carboxylic acids in distilled and river water,(141) polynuclear aromatics and su[illegible]tuted phenols in distilled water,(258-260) alkylsulfonic acids, dyes, and steroids in drinking water(261,262) and substituted aliphatics and aromatics in distilled water.(263)

The Ambersorb XE-340 resins have been investigated as sorbents for trihalomethanes. These resins have been compared to activated carbon and show very high affinities for chloroform.(264,265)

Table 18 summarizes operating parameters applied to sorbent columns during the concentration of organic analytes from water.

Sample Types

Sorbent columns, particularly XAD, are best suited to analyzing clean water types, *i.e.*, drinking waters. Particulates in turbid waters may cause severe clogging problems and head pressure changes in the column resulting in variable flow rates. Unfortunately sorbent columns only concentrate dissolved organic species, often causing serious difficulties if high particulate or colloidal loadings are present.

Waters containing highly concentrated contaminants may quickly saturate resin capacity such that accurate quantitation cannot be performed.

Advantages and Disadvantages

The use of sorbent columns for analysis of organic compounds in water offers a number of advantages over batch and continuous liquid-liquid extraction. First, with the use of these columns, it is possible to handle a large volume of sample (even thousands of liters) conveniently; therefore, the method is extremely sensitive. Also, if an experimental setup of sample reservoir, pump, sorption column, and collection tank could be properly constructed, the procedure would require very little attention and therefore would not be labor intensive. Finally, the choice of sorption material, sample conditions and eluting solvent permits the development of methods which are as general or as specific as necessary for the analysis of organic compounds in water.

While the Amberlite XAD resins look promising for use in sorbent columns, further developmental work is necessary if they are to be used routinely. One difficulty is due to the use of ether or dichloromethane as an eluting solvent. Since both of these solvents are immiscible with the water remaining on the surfaces of the sorbent particles, recovery of the adsorbed compounds can be adversely affected by the inability of the eluting

Table 18. SOME PARAMETERS IN RECENT USE OF MACRORETICULAR RESINS FOR WATER SAMPLING(209)

Resin	Compound Type	Method of Desorption	Solvent	% Recoveries
XAD-2, XAD-7	Model Compounds	Elution	$(Et)_2O$	60-90
XAD-2, XAD-7	Model Compounds	Elution	*	23-100
XAD-4	Model Compounds	Thermal	--	>80
XAD-4	Model Compounds	Elution	Acetone	>85
XAD-2	Chlorinated Pesticides	Elution	$(Et)_2O$	$\geq$89
XAD-2	PAH	Soxhlet	$MeCl_2$	45-76
XAD-2, XAD-4	Trihalomethanes	Elution	$(Et)_2O$	$\geq$60
XAD-4	Chlorinated Pesticides/PCB	Elution	$(Et)_2O/\underline{n}\text{-}C_6H_{14}$	$\geq$70
XAD-4	Trihalomethanes	Elution	EtOH	-85
XAD-4, XAD-7	Phenols	Elution	$Acetone/H_2O$	NR
IR-45, IRA-93				
IRO-900	Phenols	Elution	4% NaOH	NR
IRA-400's	Phenols	Elution	0.5-1.5%, NaOCl	NR
A-26	Phenols	Elution	$HCl/Acetone/MeCl_2$	80-95
Tenax GC®	Chlorinated Pesticides/PCBs	Elution	$(Et)_2O$	~90
Tenax GC®	Chlorinated Pesticides/PCBs	Elution	$(Et)_2O$	$\geq$70
XE-340	Trihalomethanes			NR
XE-348	Trihalomethanes			NR

*Elution with $(Et)_2O$ or $CO_3^{=}$ followed by OH^- followed by MeOH.
NR = Not investigated.

solvent to contact them. Attempts to remove the water by drying the column with a stream of inert gas or gentle heating may result in loss of volatile species. Parameters of adsorption and desorption have not been completely delineated and often organic material cannot be removed from the resin. Resin columns degrade when dry, and may give severe contamination if not wetted at all times. This can be a particularly troublesome problem if elution of organics is not performed immediately. Lastly, as already mentioned, sorbent columns will not extract organics from particulates.

Conclusions

There is a need for additional work to optimize the utility of sorbent columns in water analysis. This work should be directed toward optimizing the volume, flow rate, pH and ionic strength of the sample for analysis for a particular compound or class of compounds. Other studies should focus on the stability of the adsorbed material on the resin. Such studies would provide information on the possibility of storing the columns after the sample has been passed through them and would open the possibility of on-site sampling and shipment of the loaded columns to the laboratory for further analysis. Prevention of contamination of the column and loss of materials of interest must also be studied. Finally, attempts should be made to devise an elution scheme for serial desorption of specific classes of compounds from the XAD resin.

Despite the many studies performed using sorbent columns, they are not commonly used for routine water analysis. However, it has been demonstrated that for clean waters with low organic loading, these materials provide a viable method for concentration.

LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction (LLE) is a widely employed method for concentrating organic compounds from a sample matrix. If the analyte of interest has a higher affinity for the extracting solvent than the sample matrix, then it will partition into the solvent. The affinity of an analyte for the solvent may be defined by the distribution coefficient (K_D)(266)

$$K_D = \frac{[S]o}{[S]w}$$

if the activity of analyte in the organic layer ([S]o) and the aqueous layer ([S]w) are at equilibrium. If K_D is known for an analyte/solvent system, then the percent of analyte extracted into the solvent phase (% E) can be calculated by:(267)

$$\% E = \frac{100\ K_d}{Kd + \frac{Vw}{Vo}}$$

where Vw and Vo are the volume of water and organic solvent used during extraction. From this equation it is obvious that high analyte recoveries during LLE depend upon either a large distribution coefficient or a small water:solvent ratio.

The choice of solvent is critical to LLE procedures. As discussed above, the solvent must have a large distribution coefficient for the compounds of interest. Extensive listings of partition coefficients are available for various solvent systems.(268) Table 19 lists partition coefficients for some easily extracted and poorly extracted compounds into chloroform, heptane, and ether. Table 20 illustrates a comparison of measured and calculated extraction efficiencies for several model compounds. Partition coefficients for all organic compounds are higher for neutral species than for compounds with an electrostatic charge. To achieve electrostatic neutrality, acids are extracted at a low pH. Conversely, bases are extracted at an alkaline pH. The current EPA Priority Pollutant Protocol(269) specifies an extraction at pH 13 to concentrate neutral and basic compounds. The water is then adjusted to pH 2 and the acids are extracted. Recoveries of 80% or greater are reported for most compounds using this procedure. However, weak acids such as phenol and cresol tend to partition into both fractions. Data have been reported for a pH 8 extraction showing high recoveries for neutral compounds, weak acids, and strong and weak bases for the single pH extraction.(211)

Ion pair extraction has also been used to extract ionic species. Using this method, the organic analyte forms an ion pair when an excess of organic counterion is added.(270) The neutral ion pair is then extracted into an organic solvent. Ion pair extraction is most commonly used in conjunction with derivatization and has been applied to the analysis of basic drugs,(271,272) fatty acids,(273,274) sulphonamide,(275) diuretics in biological fluid, and ethylenethiourea(276) in water samples.

Table 19. SOLVENT: WATER PARTITION COEFFICIENTS(209)

Compound	$CHCl_3 : H_2O$	Heptane: H_2O	Ether: H_2O
Efficiently Extracted			
Propyl Ether	580	34	18
Hexyl Amine	490	30	16
Butyl Mercaptan	1,200	98	34
Benzene	460	24	15
Chlorobenzene	6,200	1,100	150
Indene	78,000	1,500	180
Acridine	20,000	9,300	575
Thiophene	301	13	10
Inefficiently Extracted			
Acetic Acid	0.03	1.0	0.4
Phenol	2	0.05	31
Benzenesulfonic acid	0.0001	0.000006	0.002
Ethylene Glycol	0.002	0.00001	0.005

Table 20. COMPARISON OF CALCULATED AND MEASURED EXTRACTION EFFICIENCIES(209)

Compound	Solvent	% Recovery	
		Calculated	Measured
Naphthalene	$CHCl_3$	99	96
Phenol	$CHCl_3$	17	28
p-Cresol	$CHCl_3$	60	67
Dibenzoguran	$CHCl_3$	100	100
Phenol	CH_2Cl_2	54[a]	75
o-Chlorophenol	CH_2Cl_2	95[a]	111
p-Nitrophenol	CH_2Cl_2	85[a]	95
2,4,6-Trichlorophenol	CH_2Cl_2	100[a]	112
Phenol	CH_2Cl_2	17[a]	20
Phenol	CH_2Cl_2	84	82

[a] Calculated values are for chloroform.

Along with having a high extraction efficiency for the analytes of interest, the extracting solvent should be immiscible with the sample, not contain contaminants which might compromise subsequent analysis, be chemically inert, be specific for the compounds of interest, and be amenable to the analytical method of choice. Since solvent evaporation is usually employed to further concentrate sample extracts, solvents with low boiling points are preferred. Benzene,(277,278) toluene,(279) pentane,(280) hexane,(281,282) and methylene chloride(279) are routinely used to extract hydrophobic compounds from water. Chloroform,(283,284) ethyl acetate,(285,279) diethyl ether,(286) methyl _t_-butyl ether,(211) and isopropyl ether(287) have been used to extract more polar analytes. For example, extraction recoveries of acrylic and methacrylic acids were less than 10% using methylene chloride but improved to greater than 80% using methyl _t_-butyl ether under identical extraction conditions.(59) Other studies have reported high recoveries for 2-pentanol using trichlorotrifluoroethane(288) and hydroquinone using methyl isobutyl ketone.(289) Table 21 lists the properties of some polar solvents which could be considered for solvent extraction procedures.

The addition of salt to the aqueous matrix will increase the activity coefficients of organic analytes to effectively increase the partition coefficient for both ionic and nonionic compounds into the organic solvent. Sodium sulfate(290,291) and sodium chloride(290,211) are most commonly used to achieve salting-out. Improved recoveries have been reported for a variety of compounds including: benzene,(289) toluene,(289) phenolics,(290,59) carboxylic acids,(59) and amines.(59) Unfortunately, the addition of salt increases the density of aqueous solutions which promotes emulsion formation when heavier than water solvents are used for extraction. This is significant since methylene chloride is commonly used as an extracting solvent.

In practice, LLE procedures are of two types - batch and continuous. Batch extractions are generally carried out by thoroughly mixing the sample and extracting solvent in a separatory funnel. The two phases are allowed to separate and the organic layer is removed. For separatory funnel techniques two minutes of vigorous shaking is usually sufficient to obtain equilibrium partition between the phases. Samples which tend to emulsify are often extracted using gentle mixing over a longer time period. Again for separatory funnel techniques, heavier than water solvents are preferred for

Table 21. POSSIBLE POLAR EXTRACTING SOLVENTS

	Physical Properties						
			Aqueous Azeotrope				
Solvent	bp (°C)	Solubility Aqueous In	% Water	bp	Dipole Moment	Density	Surface Tension
1-butanol	118	20.5%	42	93°C	1.75	.86	24.6
2-butanol	110	44%	27	87°C	-[a]	.806	23.4
isobutyl alcohol	108	17%	33	90°C	1.79	.801	22.9
t-butyl alcohol	82	inf.	12	80°C	1.66	.78	20.0
1-pentanol	138	7.5%	54	96°C	1.7	.815	25.6
2-pentanol	119	11.8%	36	92°C	1.66	.809	24.0
3-pentanol	115	8.3%	36	92°C	1.64	.820	24.6
2-methyl-1-butanol	129	9%	41	94°C	-	.819	25.1
isoamyl alcohol	130	10%	50	95°C	1.82	.810	24.8
t-amyl alcohol	102	23%	28	87°C	1.7	.801	22.8
diethyl ether	35	1.5%	1.3	34°C	1.15	.713	20.25
methyl t-butyl ether	55	1.5%	4	53°C	1.32	.741	-
di-i-propyl ether	68	0.6%	5	62°C	1.22	.725	17.34
3-pentanone	102	2.6%	14	83°C	2.82	.814	25.3
MIBK	116	1.9%	26	88°C		.801	23.6
ethyl formate	54	17%	5	53°C	1.94	.92	24.4
propyl formate	80	3%	23	72°C	1.89	.91	29.5
methyl acetate	56	8%	3	56°C	-	.93	24.8
ethyl acetate	77	3%	85	70°C	1.88	.90	23.4
propyl acetate	101	3%	14	82°C	1.78	.893	24.3
isopropyl acetate	88	2%	11	76°C	-	.871	22.1
dichloromethane	40	0.2%	1.5	38°C	1.14	1.33	28

[a] Not available.

easy handling. Exhaustive extraction procedures can involve extracting 1 L aqueous sample as many as three times with 200 to 250 mL of organic solvent each time.(211) The use of large solvent volumes is essential for polar compounds with low affinity for organic solvents; *i.e*, amines, alcohols, hydroquinone, phenols, and nitro compounds. But the use of large solvent volumes several disadvantages:(291) a concentration step is required to remove most of the solvent to improve sensitivity; impurities in the solvent are also concentrated during the concentration step; the more volatile compounds may be lost during evaporation; contamination and sample losses are more probable because of sample handling and transfers; and the cost of analysis increases because more solvent is used and the concentration step adds to the time per analysis. For compounds which partition readily into organic solvents these problems can be circumvented using microextraction techniques. Typically, sample to solvent ratios of 100 to 500 with total organic solvent volumes of 100 to 1000 µL have been used. Investigations evaluating the effects of extracting solvent, vessel configuration, sample to solvent ratio, salting out, and extraction time have been performed for the microextraction procedure.(267,289,291,292-293) This technique should be applicable to analyzing hydrophobic compounds in water samples. However, special vessels are required, more aggressive shaking is necessary to establish equilibrium, only lighter than water solvents can be used and problems with phase separations may be more severe for small solvent volumes.(291)

In continuous LLE techniques, mixing is carried out automatically for extended periods of time. The apparatus for continuous LLE is designed to recycle the extracting solvent through the sample numerous times.(294,295) Modifications(296-301) of this design allow for charging the extractor with fresh solvent. An extensive review of continuous liquid-liquid extractors has been compiled.(302) Continuous LLE has advantages(79) over batch operation due to continuous performance, minimal problems with emulsions, labor savings, consistent sample handling, capability of sampling large volumes, and high recoveries.(303,304) However, batch LLE is still the method of choice in many laboratories, probably because special equipment is not required and higher sample throughput can be achieved.

Compound Types and Recovery Data

Table 22 shows the applicability of LLE to analysis of organic compounds in aqueous samples. In this table, recoveries for various classes of compounds are given as a function of molecular weight. As seems apparent from this table, high recoveries are reported.

Most published analytical methods involving LLE isolate organic compounds which are semivolatile and nonvolatile, that is, which cannot be purged from the sample with a stream of inert gas. However, one procedure has been reported in which volatile, low molecular weight organohalides are extracted from drinking water using pentane, isooctane, or methylcyclohexane.(305) This LLE procedure has been thoroughly studied and optimized with respect to sample volume, pH, ionic strength, and solvent-to-sample ratio. This method using LLE results in the recovery of 90-95 percent of these compounds at the parts-per-billion level using electron capture detection. Tetralin extraction has also been used for volatile analysis. Tetralin, a high boiling point solvent which elutes from the chromatographic column after volatile organics, effectively removes solvent interferences.

Sample Types

Much time and effort has gone into optimizing liquid-liquid extraction methods. Applications of LLE procedures include determination of N-nitroso compounds in deionized water,(306,307) polycyclic aromatic hydrocarbons in coal process streams,(308) chlorinated aliphatics in surface waters,(309) substituted phenols in sewage and wastewater,(310) polychlorinated biphenyls in tap and river water,(311,312) chlorinated pesticides in a variety of water samples,(313-320) organophosphorus pesticides in a number of aqueous matrices,(321-323) and a variety of other pesticides in water.(324-331)

Advantages and Disadvantages

LLE is a simple, rapid, and rather clean extraction procedure. It has been well studied in terms of organic recoveries and applicability to hydrophobic compounds. The limiting factor for all extraction methods is the distribution coefficient of the substances of interest between the water and the solvent. For polar or slightly polar substances, this distribution is not very satisfactory and these compounds are isolated with poor efficiency by LLE methods. Another drawback of this technique is that partitioning of organic compounds between the aqueous sample and the solvent may not be

Table 22. PERCENT RECOVERIES BY SOLVENT EXTRACTION

<table>
<tr><th rowspan="2">Compound Types</th><th colspan="6">Molecular Weights</th></tr>
<tr><th>50</th><th>100</th><th>150</th><th>200</th><th>250</th><th>300</th></tr>
<tr><td>1. Strong Acids (pKa >6)</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Phosphonic</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Sulfonic</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Carboxylic</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Phenols</td><td></td><td></td><td colspan="2">50-75</td><td></td><td></td></tr>
<tr><td>2. Quarterary Nitrogen and Phosphonium Compounds</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>3. Amino Acids</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>4. Water Soluble Alcohols</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Carbohydrates</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Alcohols</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>5. Organometallics</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>6. Basic Nitrogen Compound</td><td></td><td>25-50</td><td>50-75</td><td></td><td></td><td></td></tr>
<tr><td>7. Weak Acids-(phenols)</td><td></td><td></td><td colspan="3">75-100</td><td></td></tr>
<tr><td>8. Water Insoluble Alcohols</td><td></td><td colspan="2">50-75</td><td></td><td></td><td></td></tr>
<tr><td>9. Polar Neutrals</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Aldehydes</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Ketones</td><td></td><td>25-50</td><td></td><td>50-75</td><td></td><td></td></tr>
<tr><td>Sulfones</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Nitro Compounds</td><td></td><td></td><td colspan="3">50-75</td><td></td></tr>
<tr><td>Nitriles</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Esters</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>10. Nonpolar Neutrals</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Ethers</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Sulfides</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Aliphatic/Aromatic</td><td>0-25</td><td>25-50</td><td colspan="4">75-100</td></tr>
<tr><td>Polynuclear Aromatics</td><td></td><td></td><td></td><td>50-75</td><td colspan="2">75-100</td></tr>
<tr><td>Pesticides and PCBs</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

efficient when the sample is contaminated at trace levels.(332) This was not of concern prior to the development of highly sensitive, selective detectors for gas chromatography and development of gas chromatography/mass spectrometry systems, which made analysis of contaminants at sub part-per-billion levels feasible. It is possible that LLE techniques are not sensitive enough to be incorporated into a scheme for analysis of organics in water at levels which are of environmental concern.

For successful liquid-liquid extraction, water and the organic solvent must be immiscible. Waters which contain high levels of surface active agents or oils tend to form emulsions during mixing. A number of classic approaches have been taken to overcome this problem, namely, heating, salting-out, centrifugation, settling, and mechanical disruption.- The effect of these techniques is usually marginal. Table 23(79) summarizes some of the literature available on both the theoretical and practical aspects of emulsions. In any analytical scheme, it is generally more desirable to prevent emulsions than to disperse them after formation.

Finally, liquid extraction techniques will accumulate all hydrophobic compounds including high molecular weight organics (*i.e.*, humic or fulvic acids, etc). These materials may cause significant background interferences during gas chromatography, as well as limit final sample concentration.

Conclusions

Despite its limitations, LLE is the most commonly used technique for the analyses of semi-volatile, hydrophobic compounds from environmental water samples. Two basic conclusions can be made regarding liquid-liquid extractions: proper solvent selection strongly influences extraction efficiency; and recovery of a particular solute can only be roughly estimated unless recovery efficiency is determined by investigations with that solute.

SOLVENT EVAPORATION

Introduction

Frequently, the isolation of organic constituents from water involves significant quantities of solvent. Prior to further separation or instrumental analysis the solvent must often be reduced to achieve the desired separation or sensitivity. Ideally, removal of the solvent should be effected without loss of solute. Several methods have been used including rotary evaporation, vacuum evaporation, free evaporation and evaporation in

Table 23. LITERATURE ON THEORETICAL AND PRACTICAL ASPECTS OF EMULSIONS

Relevant Material	References
(1) Elementary treatment of surface treatment and particle size with respect to emulsion formation.	G. M. Sutheim. Introduction to Emulsions. Chemical Publishing Co., Inc., Brooklyn, NY, 1947.
(2) Theoretical treatment of the parameters which affect the stability of emulsions, i.e., surface potential, diffusion, solvation barriers, etc. On the basis of these parameters the conditions necessary for breaking or inverting an emulsion are described.	J. T. Davies. Emulsions. Recent Progress in Surface Science, 2, 129-167 1964.
(3) The effect of a "wetting" agent in breaking an emulsion stabilized by another emulsifying agent is described. The system described is salt water in fuel oil emulsion.	A. S. C. Lawrence. The Breaking of Oil Emulsions with Synthetic Detergents. Chemistry and Industry, 615-617, 1948.
(4) Experimental evidence is given for inversion of oil/water emulsions where the oil was CCl_4, $CHCl_3$, ethyl ether, benzene, and xylene. Parameters which were varied were the soap (sodium stearate or potassium laurate), salt concentration, and base concentration.	H. V. Tarter, R. E. Lothrop and G. F. Pettengill. The Effects of Some Electrolytes on the Inversion of Emulsions. J. Phys. Chem., 34, 373-378, 1930.
(5) Detailed theoretical and experimental treatment of droplet coalescence under various shear and electrical fields as well as droplet charges.	R. S. Allan and S. G. Mason, Particle Motions in Sheared Suspension XIV Coalescence of Liquid Drops in Electrical and Shear Fields. J. Colloid Sci., 17, 363-408, 1962.
(6) Includes a chapter on "Theory of Emulsions: Creaming, Inversion, and Demulsification." This chapter discusses the role of surface active agents in emulsions, inversions, and several postulated models for the process of inversion. The chapter on demulsification is primarily practical and deals with specific industrial processes where demulsification is important including treating wool scouring wastes.	P. Becher. Emulsions: Theory and Practice. Reinhold Publishing Corp., NY, USA, 1957.

(continued)

Table 23 (cont'd.)

Relevant Material	References
(7) A technique for increasing the coalescence of emulsions on solid surfaces is presented. Primary limitations are ineffectiveness at high surfactant concentration when the densities of the two liquids are similar.	R. E. Sparks, I. D. Stafford. Continuous Breaking of Emulsions by Coalescence on Supported Liquid Films in Proceedings of the 25th Industrial Waste Conference, Purdue University, 1970. Part Two.
(8) Contains short sections on demulsifying agents, antifoaming additives and coagulation, breaking and creaming of emulsions.	A. M. Schwartz, I. W. Perry and J. Berch. Surface Active Agents and Detergents, Volume II. Interscience Publishers, Inc., New York, 1958.
(9) Experimental evidence given for increased emulsion stability for some bimolecular complexes at oil/water interfaces.	J. H. Schulman and E. G. Cockbain. Molecular Interactions at Oil/Water Interfaces, Part I. Molecular Complex Formation and the Stability of Oil in Water Emulsions Trans. Faraday Soc., 36, 651-661, 1940.
(10) Some experimental evidence given for the condifor the inversion of oil/water emulsions to water/oil emulsions and speculations as to the mechanism.	J. H. Schulman and E. G. Cockbain, Molecular Interactions at Oil/Water Interfaces. Part II Phase Inversion and Stability of Water in Oil Emulsions. Trans. Faraday Soc., 36, 651-661, 1940.
(11) Experimental and theoretical treatment of the effects of ionic strength on the surface properties of sodium dodecyl sulfate and sodium octadecyl sulfate.	B. A. Pethica and A. V. Few. The Surface Potentials of Long Chain Sulphates and Their Relation to Dispersion Stability. Discussions of the Faraday Soc., 18, 258-267, 1954.

a Kuderna-Danish concentrator, with the latter being, by far, the most popular. Insofar as solvent evaporation concentrates all solutes indiscriminately, the solvent itself must be extremely pure.(108) Concentration of solvent impurities could prevent accurate identification and quantitation of components of interest by interfering with gas chromatographic analysis.

Rotary Evaporation

Solvent removal via rotary evaporation basically involves vacuum distillation of the solvent from a revolving flask either at room temperature or some slightly elevated temperature. Polynuclear aromatics (PNAs) have been concentrated from cyclohexane by this technique.(333) Sporadic violent boiling ("bumping") is a problem but can be controlled by employing careful conditions of rotation speed, flask geometry, temperature and vacuum. Methylene chloride was effectively removed from pesticide extracts by slow rotation of a Kuderna-Danish (K-D) flask and receiver at a 20° angle, 125 mm Hg and 35°C.(334) In an effort to decrease the number of manual transfers involved in processing a sample for pesticide residue analysis, a double reservoir rotoevaporator vessel was used to collect and concentrate sample. Good recoveries were achieved with minimum sample handling.(336) Comparison of rotary evaporation to Kuderna-Danish techniques for a variety of polar and nonpolar organics have shown comparable recoveries between the two techniques. Better precision was achieved using rotary evaporation.(59)

Vacuum Evaporation

Vacuum evaporative methods are very similar to rotary evaporation, except that much smaller solvent volumes are involved. These methods differ only in the mode of agitation and heating of the sample. The agitation serves to decrease the film thickness of the fluid, increase the surface area exposed to the vacuum and to reduce bumping during release of dissolved gases.(335) Several types of agitation have been used including centrifugation, vortexing, and shaking.

Solvent removal by vacuum centrifugation involves a volume of 1-5 mL, centrifuged at 1200 or 2000 rpm under an applied vacuum. Infrared heating can be used to increase volatility. Vortexing and shaking(2) provide for sample warming by immersion of the sample tube in a heated block or bath. In each case a vacuum pump is employed and care must be exercised to prevent sample contamination from the pump, generally through use of a cryogenic trap.

As with rotary evaporation, vacuum evaporation techniques suffer from solute losses by volatilization and are, therefore, applicable to solutes of low volatility.

Kuderna-Danish Concentrator

The most frequently used solvent concentration method employs the Kuderna-Danish (K-D) evaporative concentrator. This apparatus consists of a pear-shaped flask, a small, graduated receiver and a Snyder or Vigreux column on top of the flask. The normal capacity of a K-D flask is up to 500 mL; however, micro-scale apparatuses are available for concentrating small volumes (< 10 mL). The solvent is boiled using a steam bath or a hot plate. The small chambers in the Snyder or Vigreux column cause refluxing which allows only evaporation of the most volatile component, generally the solvent. Only solvents with boiling points less than approximately 95°C can be evaporated using a steam bath. Higher boiling solvents (e.g., toluene) have been evaporated from a flat-bottomed boiling flask topped with a Snyder column using a hot plate;(337) however, in the absence of a small, graduated receiver, caution must be used to avoid reducing the volume too near dryness.

K-D concentration has been used for many different solute-solvent systems. The most successful concentrations occur for quite volatile solvents and relatively nonvolatile solutes including Kepone® in methanol/benzene,(338) pesticides and PCBs in methylene chloride/hexane,(36) and polychloronaphthalenes in toluene.(337) As the volatility of the solute increases so does the potential for evaporative losses. Ten to twenty percent of Aroclor 1016 was lost during evaporation of methylene chloride(96) while 58% of trichloroethylene was lost during evaporation of Freon TF®.(339) It has been suggested that such losses can be assessed and compensated for by inclusion of internal standards prior to evaporative concentration,[1] with the condition that the standards be similar in volatility to the compounds being determined.

A rather extensive study on parameters which affect solute recovery during K-D concentration of compounds of various classes from diethyl ether has been performed.(210) No effects were found from mode of heating, surface activity of glassware, use of boiling chips, or type of column (Snyder or Vigreux). Vessel shape, however, was significant, since continuous rinsing of the interior walls of the flask by the solvent is critical in minimizing evaporative solute losses. The rate of evaporation also affects solute recovery; higher losses of priority pollutants have been observed at slower evaporation rates than at faster rates.

During the analysis of hexachlorocyclohexane in water, a Kuderna-Danish evaporator was modified to include a built-in distillation trap below the condensing portion of the Synder column. Mean recoveries for hexane solutions of the test compound were substantially improved by this technique.(340)

Free Evaporation

Free evaporation, where solvent is removed by blowing a gas stream over the liquid surface, is predominantly used for further evaporation of small solvent volumes and is applicable only to compounds of very low vapor pressure. As high as 80% losses have been observed using this technique.(210) In a study of recovery of chloronaphthalenes during concentration of toluene, 68, 77, 39 and 25% losses of mono-, di-, tri-, and tetrachloronaphthalenes, respectively, were observed at 45°C whereas no significant losses were observed at 24°C. Nevertheless, in most cases a more efficient concentration of small volumes can be achieved with a micro-scale K-D apparatus.(96)

Summary

Tables 24 and 25 summarize recovery data for a range of organic analytes determined using selected evaporation techniques.(302) Results of this study indicate best recoveries can be achieved using a Kuderna-Danish concentration followed by nitrogen flow with a modified Snyder column.

REFERENCES

1. Headspace Analysis: A Quick Qualitative Technique for Volatile Organic Compounds, U.S. Environmental Protection Agency, Athens, GA, HVO 1/75.
2. Kaiser, K. L. E., B. G. Oliver, Anal. Chem., 48, 2207 (1976).
3. Chian, E. S. K., P. P. K. Kuo, W. T. Cooper, W. F. Cowan, R. C. Fuentes, Environ. Sci. Technol., 11, 283 (1977).
4. Bruner, F., C. Canulli, M. Possanzini, Anal. Chem., 45, 1790 (1973).
5. deSouza, T. L. C., S. P. Bhatia, Anal. Chem., 48, 2234 (1976).
6. Miller, D. L., J. S. Woods, K. W. Grubaugh, L. M. Jordon, Environ. Sci. Technol., 14, 97 (1980).
7. Pellizzari, E. D., R. A. Zweidinger, M. D. Erickson, Environmental Monitoring Near Industrial Sites, Brominated Chemicals, U. S. Environmental Protection Agency, EPA 560/6-78-002, 296 (1978).

Table 24. SUMMARY OF MACRO EVAPORATION TECHNIQUES WITH METHYLENE CHLORIDE AS SOLVENT

Compounds	Kuderna Danish	Rotary Evaporation	Hot Plate Evaporation	Nitrogen Blowdown
2-chloroethyl vinyl ether	ND[a]	ND	73(12)	ND
1-nitrobutane	ND	ND	78(17)	ND
m-dichlorobenzene	85[b](7)[c]	78(4)	77(10)	83(6)
bix(2-chloroethyl)ether	74(14)	58(9)	74(12)	76(9)
phenol	89(11)	83(5)	82(21)	101(14)
hexachlorocyclopentadiene	ND	ND	ND	ND
fluorene	85(9)	75(15)	82(16)	92(10)
lindane	84(13)	70(24)	104(22)	101(10)
Mean	83(7)	73(14)	81(14)	91(12)
Time required (min.)	10-15	15-20	30-35	120

[a] No data.

[b] Recovery (%).

[c] CV (%).

Table 25. SUMMARY OF MICRO EVAPORATION TECHNIQUES

	Methylene Chloride						15% Methylene Chloride in Hexane					
	Micro Kuderna-Danish		Nitrogen Blowdown With Column		Nitrogen Blowdown Without Column		Micro Kuderna-Danish		Nitrogen Blowdown With Column		Nitrogen Blowdown Without Column	
Compound	Recovery(%)	CV(%)	Recovery(%)	CV(%)	Recovery(%)	CV(%)	Recovery(%)	CV(%)	Recovery(%)	CV(%)	Recovery(%)	CV(%)
2-chloroethyl vinyl ether	ND[a]		ND		ND		ND		ND		ND	
1-nitrobutane	47	(8)	57	(9)	56	(4)	ND		ND		ND	
m-dichlorobenzene	76	(5)	88	(8)	77	(10)	61	(3)	25[b]	(12)	30	(23)
bis(2-chloroethyl)ether	77	(3)	87	(8)	78	(5)	93	(3)	73	(14)	77	(3)
phenol	77	(5)	89	(9)	81	(4)	81	(14)	36	(17)	50	(12)
fluorene	91	(8)	89	(4)	81	(4)	90	(7)	83	(6)	86	(5)
lindane	74	(11)	96	(4)	85	(6)	78	(9)	92	(6)	94	(7)
Mean	74	(19)	84	(17)	76	(13)	81	(16)	62	(48)	67	(40)
Time Required (min) each	10-12		10-15		10-15		25-30		10-15		10-15	

8. Drozd, J., J. Novak, J. Chromatogr., 152, 55 (1978).

9. Kolb, B., P. Pospisil, T. Borath, M. Auer, High Resolut. Chromatogr. Commun., 2, 283 (1979).

10. Meyer, T. Acta. Pharmacol. Toxicol., 43, 164 (1978).

11. Drozd, J., J. Novak, J. Chromatogr., 136, 37 (1978).

12. Drozd, J., J. Novak, J. Chromatogr., 158, 471 (1978).

13. McAuliffe, C. D., Chem. Technol., 1, 46 (1971).

14. McAuliffe, C. D., Environ. Anal., 3, 267 (1977).

15. Widonski, J., W. Thompson, Chromatogr. Newsl., 7, 31 (1979).

16. Kolb, B., P. Pospisil, M. Jaklin, D. Boege, Chromatogr. Newsl., 7, 5 (1979).

17. Dietz, E. A., K. F. Singley, Anal. Chem., 51, 1809 (1981).

18. Hachenberg, H., A. P. Schmidt, Gas Chromatography Headspace Analysis, Heyden, London, 1977, 350 pp.

19. Bassette, R., S. Ozeris, C. H. Whitnah, Anal. Chem., 34, 1540 (1962).

20. Cowen, W., W. J. Cooper, J. W. Highfill, Anal. Chem., 47, 2483 (1975).

21. Vitenberg, A. G., B. V. Ioffe, V. N. Borisov, Chromatographia, 7, 610 (1974).

22. Friant, S. L., I. H. Suffet, Anal. Chem., 51, 2167 (1979).

23. Kolb, B., P. Pospisil, M. Jaklin, D. Boege, Chromatogr. Newsl., 7, (1979).

24. Smith, J. S., D. T. Burkett, J. M. Hanrahan, Determination of Hexachloroacetone and Hexafluoroacetone in Industrial Wastewaters, Allied Chemical Corporation, Corporate Research Center, Morristown, NJ.

25. Maiorino, R. M., A. J. Gandolfi, L. G. Sipes, J. Anal. Toxicology, 4, 250 (1980).

26. Breimer, D., H. Ketelaars, J. M. Van Rossum, J. Chromatogr., 88, 55 (1974).

27. Tomita, B., S. Ohonuma, T. Shoka, N. Hamamury, Y. Ose, Eisei Kaguku, 24, 187 (1978).

28. Zuccato, E., F. Marcucci, R. Fanelli, E. Mussini, Xenobiotica, 9, 27 (1979).

29. Smith, J. S., D. T. Burkett, J. M. Hanrahan, ASTM Spec. Tech. Publ., STP 686, 251 (1978).

30. Chlorbowska, Z., A. Mady, Z. Zagadnien Krym, 12, 23 (1977).

31. Von Wartburg, J. P., M. Ris, Experientia, 35, 1682 (1979).

32. Jone, D. J., J. Pharmacol. Methods, 1, 155 (1978).

33. Hysert, D. W., N. M. Morrison, A. M. Jamieson, J. Am. Soc. Brew. Chem., 37, 30 (1979).

34. Foo, L. Y., M. Kingsford, L. J. Porter, W. A. Thomas, Rep-N.Z., Dep. Sci. Ind. Res., Chem. Div., C. D. 2274, 19 pp. (1978).

35. Kojima, M., Y. Nakano, Haggo Kogaku Kaishi, 56, 760 (1978).

36. Proposed Protocols for Measuring E.P.A. Priority Pollutants in Sewage and Sludge, U.S. Environmental Protection Agency, August (1978).

37. Bellar, T. A., J. J. Lichtenberg, The Determination of Volatile Organic Compounds at the μg/L Level in Water by Gas Chromatography, U.S. Environmental Protection Agency, EPA-670/4-74-009, 33 pp. (1974).

38. Bellar, T., J. J. Lichtenberg, J. W. Eichelberger, Environ. Sci. Technol., 10, 926 (1976).

39. Kuo, P. P., E. S. K. Chian, F. B. DeWalle, and J. H. Kim, Anal. Chem., 49, 1029 (1977).

40. Mieure, J. P., G. W. Mappes, E. S. Tucker, and M. W. Dietrich, in The Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, Inc., Ann Arbor, MI, 113 (1976).

41. Kopfler, F. C., R. G. Melton, R. O. Lingg, and W. E. Coleman, ibid., 81 (1976).

42. Ranstad, T., and T. J. Nestrick, Water Research, to be published.

43. Voznakova, Z., M. Popi, and M. Berka, J. Chromatogr. Sci., 16, 123 (1978).

44. Sievers, R. F., R. H. Shapiro, H. F. Walton, G. A. Eiceman, R. Barley, in High Resolution Gas Chromatography, S. P. Cram, ed., Academic Press, (1978).

45. Mieure, J. P., M. W. Dietrich, J. Chromatogr. Sci., 11, 550 (1973).

46. Badley, J. H., and R. C. Heaton, Ecolibrium, 7, 4 (1978).

47. Keith, L. H., K. W. Lee, L. P. Provost, Presented at Symposium on Measurement of Organic Pollutants in Water, ASTM, Denver, CO, 44 (1978).

48. Pellizzari, E. D., Analysis of Organic Air Pollutants by Gas Chromatography and Mass Spectrometry, EPA Project No. 68-02-2262, 1977, 225 pp.

49. "Purgeables - Method 624," Federal Register, 44, No. 233, 69532, Monday, December 3, 1979.

49. Sheldon, L. S., J. P. Goforth, and E. D. Pellizzari, Master Analytical Scheme:Analysis of Low Molecular Weight, Polar Organics, ACS National Meeting, Las Vegas, Nevada, March 1982.

50. Spraggins, R. L., R. G. Oldham, C. L. Prescott, K. J. Baughman, in Advances in the Identification and Analysis of Organic Pollutants in Water, Volume 2, L. H. Keith, ed., Ann Arbor Science, Inc. Ann Arbor, MI, 447 pp. (1981).

51. Pellizzari, E. D., R. A. Zweidinger, M. D. Erickson, Environmental Monitoring Near Industrial Sites: Brominated Chemicals, Part I, U. S. Environmental Protection Agency, EPA-560/6-78-002, 296 (1978).

52. Lee, K. Y., D. Nurok, A. Zlatkis, J. Chromatogr., 158, 377 (1978).

53. Novak, J., J. Janak, J. Golias, NBS Spec. Publ., 1979, 519, 739-16.

54. Eklund, G., B. Josefsson, C. Roos, Chromatogr. Newsl., 6, 39 (1978).

55. Trussel, A. R., T. Y. Lieu, J. C. Moncur, Op Cit., L. H. Keith, ed., Volume 1, 171 (1981).

56. Pellizzari, E. D., Identification of Components of Energy Related Wastes and Effluents, U. S. Environmental Protection Agency, EPA-600/7-78-004, 524 pp. (1978).

57. UNACON liter.

58. Janak, J., J. Ruzickova, J. Novak, J. Chromatogr., 99, 689 (1974).

59. Zweidinger, R. A., L. S. Sheldon, J. W. Hines, L. C. Michael, "Analytical Procedures for Proposed Toxics in Wastewaters and Sludges," Final Report, EPA Contract No. 68-03-2845 (1982).

60. Pellizzari, E. D., Master Scheme for the Analysis of Organic Compounds in Water, Interim Report, EPA Contract No. 68-03-2704, 1979.

61. Rose, M. E., B. N. Colby, Anal. Chem., 51, 2176 (1979).

62. Erickson, M. D., M. K. Alsup, P. A. Hyldburg, Anal. Chem., 53, 1265 (1981).

63. Pfaender, F. K., R. B. Jones, A. A. Stevens, L. Moore, J. R. Hass, Environ. Sci. Technol., 12, 438 (1978).

64. Pellizzari, E. D., Preliminary Assessment of Halogenated Organic Compounds in Man and Environmental Media, Report No. 6, U. S. Environmental Protection Agency, Contract No. 68-01-4731, 52 pp., May (1978).

65. Pellizzari, E. D., Ibid, Report No. 8, 35 pp., July (1978).

66. Beggs, D. P., Automated Analysis of Organic Pollutants in Water via GC/MS, report, Hewlett-Packard, Palo Alto, CA, 1978.

67. Burgett, C. A., L. E. Green, Hewlett-Packard Application Note ANGC 5-75 (1975).

68. Jennings, W. G., R. Wohleb, M. J. Lewis, J. Food Sci., 37, 69 (1972).

69. May, W. E., S. N. Chesler, S. P. Cram, B. H. Gump, H. S. Hertz, D. P. Enangonio, S. M. Dyszel, J. Chromatogr. Sci., 13, 535 (1975).

70. Ewing, B. B., E. S. K. Chian, J. C. Cook, C. A. Evans, P. K. Hopke, E. G. Perkings, Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters, Report No. 1, U. S. Environmental Protection Agency, Contract No. 68-01-3234, 62 pp. (1975).

71. Meiggs, T. O., Volatile Organic Compounds by GC/MS, Attachment III-VIII, U. S. Environmental Protection Agency, Denver, CO, 49 (1978).

72. Dowty, B., D. Carlisle, J. L. Laseter, Environ. Sci. Technol., 9, 762 (1975).

73. Dowty, B., J. Laseter, Anal. Lett., C117, 25 (1975).

74. Dowty, B., D. Carlisle, J. L. Laseter, Science, 187, 75 (1975).

75. Lingg, R. D., R. G. Melton, F. C. Kopfler, W. E. Coleman, D. E. Mitchell, J. Amer. Water Works Assoc., 69, 605 (1977).

76. Pellizzari, E. D., N. P. Castillo, Symposium on Measurement of Organic Pollutants in Water and Wastewater, ASTM Meeting, Denver, CO, June (1978).

77. Pellizzari, E. D., N. P. Castillo, S. Willis, D. Smith, J. T. Bursey, Symposium on Potential Health and Environmental Effects of Synthetic Fossil Fuel Technology, Gatlinburg, TN, September (1978).

78. Pellizzari, E. D., N. P. Castillo, S. Willis, D. Smith, J. T. Bursey, Fuel Chem., in press.

79. Erickson, M. D., R. A. Zweidinger, Techniques for Handling Emulsions and Solvent Concentrations in Priority Pollutant Analysis, Literature Review, U. S. Environmental Protection Agency, Contract No. 68-03-2759, (1978).

80. Dunlap, W. J., J. F. McNabb, M. R. Scalf, R. L. Cosby, Sampling for Organic Chemicals and Microorganisms in the Subsurface, U. S. Environmental Protection Agency, EPA-600/2-77-176, 27 p. (1977).

81. Beggs, D. P., Hewlett-Packard Application Note, AN176-24 (1978).

82. Ground Water Research Branch, Preliminary Survey of Toxic Pollutants of the Muskegon Wastewater Management System, report, U. S. Environmental Protection Agency, Ada, Oklahoma, 22 pp. (1977).

83. Chriswell, C. D., J. S. Fritz, J. Chromatogr., 136, 89 (1977).

84. Rivera, J., M. R. Cuberes, J. Abaiges, Bull. Environ. Contam. Toxicol., 18, 624 (1977).

85. Smillie, R. D., T. Sakuma, G. A. Duholke, J. Environ. Sci. Health, 13, 187 (1978).

86. Alberti, J. B. Jonke, Z. Wasser Abwasser Forsch., 8, 140 (1975).

87. Bertsch, W., E. Anderson, G. Holzer, J. Chromatogr., 112, 701 (1975).

88. Alford, A., Biomed. Mass Spectrom., 4, 1 (1977).

89. Novak, J., J. Klutechky, V. Jubelka, J. Mostecky, J. Chromatogr., 76, 45 (1973).

90. Karasek, F. W., Ind. Res. Develop., 113 (1978).

91. Smillie, R. D., A. A. Nicholson, O. Meresz, G. A. Duholke, V. Rees, K. Roberts, C. Fung, Organics in Ontario Drinking Waters, Part II. A Survey of Selected Water Treatment Plants, Report, Ontario Ministry of the Environment, Rexdale, Ontario, Canada, 79 pp. (1977).

92. Harris, J. A., P. Levins, Interim Procedures for Level 2 Sampling and Analysis of Organic Materials, U. S. Environmental Protection Agency, EPA-600/7-78-016, 84 pp. (1978).

93. McKinney, J. D., R. R. Maurer, J. R. Hass, R. O. Thomas, op. cit., in L. H. Keith, ed., 417 (1976).

94. Nicholson, A. A., O. Meresz, B. Lemyk, Anal. Chem., 49, 814 (1976).

95. Nicholson, A. A., O. Meresz, Organics in Ontario Drinking Waters, Part I. The Occurrence and Determination of Free and Total Potential Haloforms, Report, Ontario Ministry of the Environment, Rexdale, Ontario, Canada, 19 pp. (1976).

96. Hall, J. R., M. N. Wass, R. A. Solomon, Presented at 176th ACS Meeting Division of Environmental Chemistry, Miami, FL, September (1978).

97. Dowty, B. J., S. R. Antoine, J. L. Laseter, Quantitative and Qualitative Analyses of Purgeable Organics by High Resolution Gas Chromatography and Flame Ionization Detection, preliminary report, University of New Orleans, New Orleans, LA.

98. Ewing, B. B., E.S.K. Chian, J. C. Cook, C. A. Evans, P. K. Hopke, E. G. Perkins, op. cit., Report No. 3, January (1976).

99. Neely, M. A., R. Greenspan, R. A. Carr, presented at 176th ACS Meeting, Division of Environmental Chemistry, Miami, FL, September (1978).

100. Novotny, M., M. L. Lee, K. D. Bartle, Chromatographia, 7, 333 (1974).

101. Novotny, M., M. L. McConnell, M. L. Lee, R. Farlow, Clin. Chem., 20, 1105 (1974).

102. Pellizzari, E. D., Acquisition and Chemical Analysis of Human Tissue, Blood, and Urine for Selected Toxic Substances, Report No. 9, U. S. Environmental Protection Agency, Contract No. 68-01-3849, 7 pp. August (1978).

103. Lee, K. W., L. H. Keith, R. G. Oldham, L. P. Provost, P. H. Lin, L. Sellman, D. L. Lewis, Presented at International Symposium on the Analysis of Hydrocarbons and Halogenated Hydrocarbons in the Environment, Ontario, Canada, 21 pp. May (1978).

104. Jennings, W. G., H. E. Nursten, Anal. Chem., 39, 521 (1967).

105. Zlatkis, A., H. A. Lichtenstein, A. Tishbee, W. Bertsch, F. Shumbo, H. M. Liebich, J. Chromatogr. Sci., 11, 299 (1973).

106. Grob, K., J. Chromatogr., 84, 255 (1973).

107. Coleman, W. E., R. G. Melton, R. W. Slater, F. G. Kopfler, S. J. Voto, W. K. Allen, T. A. Aurand, J. Am. Water Works Assoc., 73, 119 (1981).

108. Grob, K., K. Grob, Jr., G. Grob, J. Chromatogr., 106, 299 (1975).

109. Grob, K., G. Grob, J. Chromatogr., 90, 303 (1974).

110. Grob, K., F. Zürcher, J. Chromatogr., 117, 285 (1976).

111. Reinhard, M., J. E. Schreiner, T. Everhart, J. Graydon, "Specific Compound Analysis by Gas Chromatography and Mass Spectroscopy in Advanced Treated Waters," NATO/CCMS Conference of Practical Application of Adsorption Techniques, Reston, VA, May 1, 1979.

112. Kransner, S. W., C. J. Hwang, M. J. McGuire, Op. Cit., L. Keith, ed., Volume 2, 689 (1981).

114. Zuircher, F., W. Giger, Vom Wasser, 47, 37 (1976).

115. Giger, W., M. Reinhard, C. Schaffner, T. Zurcher, Op. Cit., L. Keith, ed., 433 (1976).

116. Coleman, W. E., W. K. Allens, R. W. Slater, S. J. Voto, R. G. Melton, F. C. Kopfler, op. cit., L. Keith, ed., Volume 2, 671 (1981).

117. Melton, R. G., W. E. Coleman, R. W. Slater, F. C. Kopfler, W. K. Allen, T. A. Aurard, D. E. Mitchell, S. J. Voto, op cit., L. Keith, ed., Volume 2, 597 (1981).

118. Stieglitz, L., W. Roth, W. Kuhn, W. Giger, Vom Wasser, 47, 347 (1976).

119. Giger, W., C. Molanr, S. Wakeham, "Volatile Chlorinated Hydrocarbons in Ground and Lake Water," in Aquatic Pollutants, O. Hutzinger, ed., Oxford, Pergamon Press, 1978.

120. Schwarzenback, R. P., E. Molnar-Kubica, W. Giger, and S. G. Wakeman, Environ. Sci. Technol., 13, 1367 (1979).

121. Schwarzenback, R. P., R. H. Bromund, P. M. Gschwend, and O. C. Zaferiau, Org. Geochem., 1, 93 (1978).

122. Fujii, T., Anal. Chem., 49, 1985 (1977).

123. Fujii, T., J. Chromatogr., 139, 297 (1977).

124. Lovelock, J. E., R. J. Maggs, R. J. Wade, Nature, 241, 194 (1973).

125. Fisher Scientific Co., Determination of Low Level Phenol in Surface and Effluent Waters, Bulletin CF-23.

126. Harris, L. E., W. L. Budde, J. W. Eichelberger, Anal. Chem., 46, 1912 (1974).

127. Onuska, F. I., Water Research, 7, 835 (1973).

128. Kubelka, V., J. Mitera, V. Rabl, J. Mostecky, Water Research, 19, 137 (1976).

129. Mikhailovskii, N. Ya., P. G. Rumyantsev, A. A. Korolev, A. P. Illnitskii, Gig. Sanit., 2, 71 (1971).

130. Fox, M. E., Environ. Sci. Technol., 7, 838 (1973).

131. McAuliffe, C., Nature, 200, 1092 (1963).

132. Melcher, R. G., V. J. Caldencourt, Anal. Chem., 52, 875 (1980).

133. Simmonds, P. G., E. Kerns, J. Chromatogr., 186, 785 (1979).

134. Nicholson, A. A., O. Meresz, Bull. Environ. Contam. Toxicol., 14, 453 (1976).

135. Smith, H. R, G. W. Tindall, Microchem. J., 24, 463 (1979).

136. Chian, E. S. K., P. P. K. Kuo, Fundamental Study on the Post-Treatment of RO Permeates from Army Wastewaters, U. S. Dept. of Commerce, NTIS AD-A035-912, 134 pp., October (1976).

137. Peters, T. L., Anal. Chem., 52, 211 (1980).

138. Veith, G. D., L. M. Kiwus, Bull. Environ. Contam. Toxicol., 17, 631 (1977).

139. Fine, D. H., D. P. Rounbehler, N. P. Sen, J. Agr. Food Chem., 24, 980 (1976).

140. McNeal, T., W. C. Brumley, C. Breden, J. Assoc. Offic. Anal. Chem., in press.

141. Nickerson, G. B., S. T. Likens, J. Chromatogr., 21, 1 (1966).

142. Maarse, H., R. E. Kepner, J. Agr. Food Chem., 18, 1095 (1970).

143. Loy, E. W., J. A. Little, D. W. Brown, J. H. M. Stephenson, Uses of Wastewater Discharge Compliance Monitoring Data, U. S. Environmental Protection Agency, Athens, GA (1975).

144. Kenmotsu, K., K. Matsunnaga, T. Ishida, Okayama-ken Karikyo Hoken Senta Nempo, 2, 164 (1978).

145. Jennings, W. G., M. Feilsoof, J. Agr. Food Chem., 25, 440 (1977).

146. Lichtenberg, J. J., IEEE Transactions on Nuclear Science, NS-22, 874 (1975).

147. Mousa, J. J., Symposium on Measurement of Organic Pollutants in Water and Wastewaters, ASTM Committee D-19, Denver, CO, June (1978).

148. Marcus, M., J. Spigarelli, H. Miller, Organic Compounds in Organophosphorus Pesticide Manufacturing Wastewaters, U. S. Environmental Protection Agency, EPA 68-03-2343, 82 pp. (1977).

149. Jeon, I. J., G. A. Reineccius, E. L. Thomas, J. Agr. Food Chem., 24, 433 (1976).

150. Cruver, J. E. in Physicochemical Processes for Water Quality Control, W. J. Weber, ed., Wiley-Interscience, New York, p. 293 (1972).

151. Cabasso, I., C. S. Eyer, E. Klein, J. K. Smith, Evaluation of Semipermeable Membrances for Concentration of Organic Contaminants in Drinking Water, U. S. Environmental Protection Agency, EPA 670/1-75-001, June (1975).

152. Cadotte, J. E., C. V. Kopp, K. E. Cibian, L. T. Rozelle, Progress Report on In-Situ-Formed Condensation Polymers for Reverse Osmosis Membranes, Office of Saline Water, U. S. Department of the Interior, 92 pp. June (1974).

153. Smith, J. K., A. J. Englande, M. M. McKown, S. Lynch, Characterization of Reusable Municipal Wastewater Effluents and Concentration of Organic

Constituents, U. S. Environmental Protection Agency, EPA 600/2-78-006, (1978).

154. Kopfler, F. C., W. E. Coleman, R. G. Melton, R. G. Tardiff, Ann. N. Y. Acad. Sci., 248, 20 (1977).

155. Sourirajan, S., Reverse Osmosis, Academic Press (1970).

156. Anderson, J. E., S. J. Hoffman, C. R. Peters, J. Phys. Chem., 76, 4006 (1972).

157. Osmonics, Inc., Econo-pure, Simple Reverse Osmosis at Reasonable Costs, EP-7602/40, Hopkins, MN (1976).

158. Deinzer, M., R. Melton, D. Mitchell, Water Research, 9, 749 (1975).

159. Hindin, E., P. J. Bennett, S. S. Narayanan, Water and Sew. Works, 116, 466 (1969).

160. Duvel, W. A., O. Helfgott, E. J. Genetilli, Presented at ACS Meeting, Division of Water, Air, and Waste Chemistry, Chicago, IL, September (1970).

161. Matsuura, T., S. Sourirajan, J. Appl. Poly Sci., 16, 2531 (1972).

162. Matsuura, T., S. Sourirajan, J. Appl. Poly. Sci., 15, 2905 (1971).

163. Kamizawa, C., H. Masuda, S. Ishizaka, Bull. Chem. Soc. Japan, 45, 2967 (1972).

164. Klein, E., J. Eichelburger, C. Eyer, J. Smith, Water Research, 9, 807 (1975).

165. Chian, E. S. K., W. N. Bruce, H. H. P. Fang, Environ. Sci. Technol., 9, 52 (1975).

166. Chian, E. S. K., A.I.Ch.E. Symp. Ser., 136, 497 (1975).

167. Matsuura, T., S. Sourirajan, J. Appl. Poly. Sci., 17, 3361 (1973).

168. Matsuura, T., S. Sourirajan, J. Appl. Poly. Sci., 16, 1663 (1972).

169. Hindin, E., P. J. Bennett, Water and Sew. Works, 116, 66 (1969).

170. Shimado, T., Fuji Jiho, 50, 294 (1977).

171. Minear, R. A., Environ. Sci. Technol., 6, 431 (1972).

172. Minear, R. A., K. A. Walanski, Investigation of the Chemical Identity of Soluble Organophosphorus Compounds Found in Natural Waters, Illinois Institute of Technology, Chicago, Illinois, Research Report No. 86, UILU-WRC-74-0086, 64 pp. (1974).

173. Minear, R. A. Investigation of the Chemical Identity of Soluble Organophosphorus Compounds Found in Natural Waters, University of Tennessee, Knoxville, Tennessee, Research Report No. 64, 152 pp. (1978).

174. Jolley, R. L., S. Katz, J. E. Mrochet, W. W. Pitt, Jr., W. T. Rainey, Chem. Technol., 5, 312 (1975).

175. Pitt, W. W., Jr., R. L. Jolley, S. Katz, op. cit., L. H. Keith, ed., p. 215 (1976).

176. Harrison, S. H., P. D. Lafleru, Anal. Chem., 9, 1685 (1975).

177. Lavrov, I. S., V. N. Ponomareva, O. M. Rozental, Ah. Prike Khim. (Leningrad), 50, 1048 (1977).

178. Bargnoux, H., D. Pepin, J. L. Charbard, T. Vedrine, J. Petit, J. Berger, Analusis, 8, 177 (1980).

179. Klockow, D., W. Bayer, W. Fargle, Z. Anal. Chem., 292, 385 (1978).

180. Teranishi, R., P. Issenberg, I. Horvistein, E. L. Wick, Flavor Research, Marcel Dekker, Inc., New York (1971).

181. Weber, W. J. in Physicochemical Processes for Water Quality Control, W. J. Weber, ed., Wiley-Interscience, New York, p. 261 (1972).

182. Helfferich, F., Ion Exchange, McGraw-Hill Book Co., Inc., New York (1962).

183. Richard, J. J., C. D. Chiswell, J. S. Fritz, J. Chromatogr., 199, 143 (1980).

184. Sheldon, L. S., S. Young, E. Pellizzari, "Development of a Master Analytical Scheme. Development of Methods for Ionic Intractables," 178th National ACS Meeting, September 1979, Washington, D.C.

185. Gebhart, J. E., J. T. Ryan, R. D. Cox, E. D. Pellizzari, L. C. Michael, L. S. Sheldon, op. cit., L. Keith, ed., Volume 1, 31 (1981).

186. Michael, L. C., R. Wiseman, L. S. Sheldon, J. T. Bursey, K. B. Tomer, E. D. Pellizzari, T. A. Scott, R. Coney, A. W. Garrison, J. E. Gebhart, J. F. Ryan, ibid, p. 87.

187. Larson, R. D., J. C. Weston, S. M. Howell, J. Chromatogr., 111, 43 (1975).

188. Siegel, A., E. T. Deegens, Science, 151, 1098 (1966).

189. "Materials, Equipment and Systems for Chromatography, Electrophoresis, Membrane Filtration and Immunochemistry," Biorad Laboratories, Richmond, CA, (1978).

190. Lee, C., J. L. Bada, Limnol. and Ocean, 22, 502 (1977).

191. Lee, C., J. L. Bada, Earth Planet Sci. Lett., 26, 61 (1975).

192. Chau, Y. K., M. E. Fox, J. Chromatogr. Sci., 9, 271 (1971).

193. Stuber, H. A. J. A. Leehneer, Fractionation of Organic Solutes in Oil Shale Retort Waters for Sorption Studies on Processed Shale, Report, U. S. Geological Survey, Denver, Colorado (1977).

194. Michael, L., Thesis. The University of North Carolina, Chapel Hill, North Carolina, (1977).

195. Webb, K. L., L. Wood in Automation in Analytical Chemistry, Technicon Symposium, New York, p. 440 (1967).

196. Aue, W. W., C. R. Hastings, K. O. Gerherdt, J. O. Pierce, H. H. Hill, R. F. Moseman, J. Chromatogr., 72, 259 (1972).

197. Larson, R. D., J. C. Weston, S. M. Howell, J. Chromatogr., 111, 43 (1975).

198. Verwey, A., C. E. Degenhardt, H. L. Boter, Chemosphere, 8, 115 (1979).

199. Junk, G. A, J. J. Richard, op. cit., L. Keith, ed., Volume 1, 295, (1981).

200. Leehneer, J. A., E. W. D. Huffman, J. Res. U. S. Geol. Surv., 4, 737 (1976).

201. Harding, B. L., K. O. Linstedt, E. R. Bennett, R. E. Paulson, Proceedings of the Second Pacific Area Chemical Engineering Congress, Denver, CO, 1, 442 (1977).

202. Gardiner, J., Analyst, 102, 120 (1977).

203. Coults, R. F., G. R. Jones, L. F. Liu, J. Chromatogr. Sci., 17, 551 (1979).

204. Fitch, W. L., P. J. Anderson, D. H. Smith, J. Chromatogr., 162, 249 (1979).

205. Gates, S. C., N. Dendramis, C. C. Sweeley, Clin. Chem., 24, 1674 (1978).

206. Hartmut, F., A. Rettenmeler, H. Weicker, G. Nicholson, E. Bayer, Anal. Chem., 54, 715 (1982).

207. Issachu, D., J. F. Holland, C. C. Sweeley, Anal. Chem., 54, 29 (1982).

208. Chriswell, C. C., R. C. Chang, J. S. Fritz, Anal. Chem., 47, 1325 (1975).

209. Harris, J. C., M. J. Cohen, Z. A. Grosser, M. J. Hayes, "Characterization of Sorbent Resins for Use in Environmental Sampling," EPA Contract No. 68-02-2150 and 68-02-3111, July 1980, 61 pp.

210. Junk, G. A., J. J. Richard, M. D. Griesser, D. Witiak, J. L. Witiak, M. D. Arguella, R. Vick, H. J. Svec, J. S. Fritz, G. V. Calder, J. Chromatogr., 99, 145 (1978).
211. Sheldon, L. S., R. A. Zweidinger, M. A. Jones, J. S. Storm, E. D. Pellizzari, The Master Analytical Scheme for Organics in Water: Extractable Organic Compounds, presented at National ACS Meeting, Las Vegas, NV, March 1982.
212. Kelsey, M., E. Mosgatelli, J. Chromatogr., 85, 65 (1974).
213. Ripley, J., D. Taylor, Analytica Chemica Acta, 46, 307 (1969).
214. Kamikubo, T., H. Narahara, Japan Patent 38,058 (1970).
215. Renberg, L., Anal. Chem., 50, 1836 (1978).
216. Schnare, D. W., J. Water Pollut. Control Fed., 51, 2467 (1979).
217. Van Rossum, P., R. G. Webb, J. Chromatogr., 139, 17 (1977).
218. Webb, R. G., "Isolating Organic Water Pollutants: XAD Resins, Urethane Foams, Solvent Extraction," EPA 660/4-75-003 (1975).
219. Musty, P. R., G. Nickless, J. Chromatogr., 100, 83 (1974).
220. Ahling, B., S. Jensen, Anal. Chem., 42, 1483 (1970).
221. Musty, P. R., G. Nickless, J. Chromatogr., 89, 185 (1974).
222. Bastos, M., D. Jukofsky, S. Mule, J. Chromatogr., 81, 93 (1973).
223. Chriswell, C. D., R. L. Ericson, G. A. Junk, K. W. Lee, J. S. Fritz, H. J. Svec, J. Amer. Water Works Assoc., 31, 669 (1977).
224. Pfaender, F. K., M. S. Shuman, H. Dempsey, C. W. Harden, WRRI Report No. 126 (1977).
225. Coburn, J. A., I. A. Valdmanis, A. S. Y. Chau, J. Assoc. Offic. Anal. Chem., 60, 224 (1977).
226. Richard, J., J. Fritz, Talanta, 21, 91 (1974).
227. Prater, W. A., M. S. Simmons, K. H. Mancy, Anal. Lett., 13, 205 (1980).
228. Chang, R. C., J. S. Fritz, Talanta, 25, 659 (1978).
229. Ryan, J. P., J. S. Fritz, J. Chromatogr. Sci., 16, 488 (1978).
230. Ryan, J. P., J. S. Fritz, op.cit., L. Keith, ed., Volume 1, 317 (1981).
231. Tateda, A., J. S. Fritz, J. Chromatogr., 152, 329 (1978).
232. Stepan, S. P., J. F. Smith, Water Research, 11, 339 (1977).
233. Chasanov, M. G., R. Kunin, F. McGarvey, Ind. Eng. Chem., 48, 305 (1956).
234. Adams, J., K. Menzies, P. Levins, Selection and Evaluation of Sorbent Resins for the Collection of Organic Components, EPA Publ. 600/7-77-0144, NTIS PB-268, 559/2SL.

235. Harvey, G. R., "Adsorption of Chlorinated Hydrocarbons from Seawater by a Crosslinking Polymer," Technical Report for the National Marine Water Quality Laboratory, EPA CZ 16020, 1972.

236. Rosen, A. A., F. M. Middleton, Anal. Chem., 31, 1729 (1959).

237. Fine, D. H., D. P. Rounbehler, F. Huffman, A. W. Garrison, N. L. Wolfe, S. S. Epstein, Bull. Environ. Contam. Toxicol., 14, 404 (1975).

238. Brans, H., F. M. Middleton, G. Walton, Anal. Chem., 23, 1160 (1951).

239. Eichelberger, J., J. Lichtenberg, J. Amer. Water Works Assoc., 63, 25 (1971).

240. Sproul, O., D. W. Ryckman, J. Water Pollut. Control Fed., 33, 1188 (1961).

241. Burnham, A. K., G. V. Calder, S. S. Fritz, G. A. Junk, H. J. Svec, R. Willis, Anal. Chem., 44, 139 (1972).

242. Bean, R. M., P. W. Rayn, R. G. Riley, Presented at 174th National ACS Meeting, Chicago, IL, (1977).

243. Richard, J. J., G. A. Junk, M. J. Avery, N. L. Nehring, J. S. Fritz, H. J. Svec, Pestic. Monit. J., 9, 117 (1975).

244. McNeil, E. E., R. Otson, W. F. Miles, F. J. M. Rajabalee, J. Chromatogr., 132, 277 (1977).

245. Suffet, I. H., L. Brenner, J. V. Radzuil, Op. Cit., L. Keith, ed., 375 (1976).

246. Osterroht, C., J. Chromatogr., 101, 259 (1974).

247. Stuermer, O. H., G. R. Harvey, Deep Sea Res., 24, 303 (1977).

248. Leo, A. C., C. Hanch, D. Elkins, Chem. Review, 71 (1971).

249. Mierzwa, S., S. Witek, J. Chromatogr., 136 105 (1977).

250. Aiken, G. R., E. M. Thurman, R. L. Malcolm, H. T. Walton, Anal. Chem., 51, 1799 (1979).

251. Dunlap, W., D. C. Shew, M. R. Scalf, R. L. Casby, J. M. Robertson, op. cit., L. H. Keith, ed., p. 453.

252. Bedford, J. W., Bull. Environ. Contam. Toxicol., 12, 622 (1974).

253. Versino, B., H. Knoppel, M. Degroot, A. Peil, J. Poelman, H. Schauenburg, H. Vissers, F. Geiss, J. Chromatogr., 122, 373 (1976).

254. Mieure, J. P., M. W. Dietrich, J. Chromatogr. Sci. 11, 559 (1973).

255. Aue, W. A., S. Kapila, C. R. Hastings, J. Chromatogr., 73, 99 (1972).

256. Weliber, A., W. M. d'Angelo, S. W. Bigelow, Evaluation of High Performance Liquid Chromatographic Packing for Concentration and Separation of Organic Materials in Water, NTIS AD-A053, 683-4ST.
257. Coburn, J. A., A. S. Chau, J. Assoc. Offic. Anal. Chem., 59, 862 (1976).
258. Stepein, L. F., J. F. Smith, Water Resaerch, 11, 339 (1977).
259. Caton, J. E., Z. K. Barnes, H. Kubota, W. H. Griest, M. P. Maskarinec, op. cit., L. Keith, ed., Volume 1, 329 (1981).
260. Landrum, P. F., J. P. Giesy, Ibid., 345 (1981).
261. Burnham, A. K., G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec, R. Willis, Anal. Chem., 44, 139 (1972).
262. Rohm and Haas Co., Amberlite XAD Macroreticular Adsorbents, Philadelphia, PA (1970).
263. Thurman, E. M., R. L. Malcolm, G. R. Aiken, Anal. Chem., 50, 755 (1970).
264. Neely, W., A Model for the Removal of Trihalomethanes from Water by Ambersorb XE-340, American Chemical Society National Meeting, Miami, FL, September (1970).
265. Mullins, R. L., J. S. Zogoski, S. A. Hubls, G. D. Allgier, A. N. Arbuckle, D. A. Welding, Effectiveness of Several Brands of Granular Activated Carbon for the Removal of Trihalomethanes from Drinking Water, ACS National Meeting, Miami, FL, September 1978.
266. Nernst, Z., J. Physik., 8, 110 (1891).
267. Rhodes, J. W., C. P. Nulton, op. cit., L. Keith, ed., Volume 1, 241 (1981).
268. Leo, A., C. Hansch, D. Elkins, Chemical Review, 71 G (1971).
269. "Base/Neutrals, Acids, and Pesticides - Method 625," Federal Register, 44, No. 233, 69540, Monday, December 3, 1979.
270. Schill, G., R. Modin, K. Borg, B. A. Persson, Ion-Pair Extraction and Ion-Pair Chromatography, in Handbook of Derivatives for Chromatography, K. Blau and G. S. King, eds., Heyden Press, London, 500 (1978).
271. Brotell, H., H. Ehrsson, O. Gyllenhall, J. Chromatogr., 78, 293 (1973).
272. Greving, J. E., J. H. Jonkman, F. Fiks, R. DeZeeuw, J. Chromatogr., 142, 611 (1977).
273. Franklin, T. C., O. Naoyuk, Anal. Lett., All, 817 (1978).
274. Gyllenhall, O. H. Brotell, P. Hartvey, J. Chromatogr., 169, 214 (1979).

275. Fagerlund, P. Hartvig, J. Chromatogr, 168, 107 (1979).
276. Singh, J., W. P. Cochrane, W. P. Scott, J. Bull Environ. Contamin. Toxicol., 23, 470, (1979).
277. Kulekova, G. S., V. E. Kirichenko, K. I. Pashkevich, Zh. Anal. Khim, 34, 790 (1979).
278. Goldberg, M., L. Delong, M. Sinclair, Environ. Sci. Technol., 5, 161 (1971).
279. Leobering, H. G., L. Weil, K. Quentin, Vom Wasser, 51, 265 (1978).
280. Glaze, W. H., R. Rawley, J. L. Burleson, D. Mapel, D. R. Scott, Op. Cit., L. Keith, ed., Volume 1, 267 (1981).
281. Kawahar, F., J. Eichelberger, B. Reed, H. Stierli, J. Water Pollut. Contr. Fed., 39, 572 (1967).
282. Murtaugh, J., R. Bunck, J. Water Pollut. Contr. Fed., 39, 404 (1967).
283. Krasnykh, A. A., Gig. Sanit., 43, 92 (1978).
284. Stoeber, I., R. Rupert, Vom Wasser, 51, 273 (1978).
285. Webster, G. R., B. L. Worobey, Int. J. Environ. Anal. Chem., 6, 197 (1979).
286. Lukas, G., K. Vyas, S. Brindle, Anal. Lett., B11, 953 (1978).
287. Fritchi, U., G. Fritchi, H. Kussmaul, Wasser Abwasser-Forsch., 11, 165 (1978).
288. Goldberg, M., L. Delong, M. Sinclair, Anal. Chem., 41, 89 (1973).
289. Thrun, K. E., J. E. Oberholtzer, op. cit., L. Keith, ed., Volume 1, 253 (1981).
290. Korenman, Y. I., R. N. Bortnikova, Zh. Anal. Khim, 34, 2425 (1979).
291. Junk, G. A., I. Ogawa, H. J. Svec., op. cit., L. Keith, ed., Volume 1, 281 (1981).
292. Rhoades, J. W., J. D. Millar, J. Agr. Food Chem., 13, 5 (1965).
293. Grob, K., K. Grob, Jr., G. Grob, J. Chromatogr. 106, 299 (1975).
294. Hoffman-LaRoche and Co., A.G., Brit. Patent 791025 (1968).
295. Morrison, G. H., H. F. Frieser, Solvent Extraction in Analytical Chemistry, John Wiley and Sons, New York, p. 86 (1966).
296. Kahn, L., C. H. Wayman, Anal. Chem., 45, 89 (1973).
297. Goldberg, M. C., L. DeLong, M. Sinclair, Anal. Chem., 45, 89 (1973).
298. Ahnoff, M., B. Josefsson, Anal. Chem., 46 (1974).

299. Shackelford, W. M., R. G. Webb, ASTM Spec. Tech. Publ., STP 686, 191 (1978).

300. Hoffman, W. A., Anal. Chem., 50, 2158 (1978).

301. Yohe, T. L., I. H. Suffet, R. J. Grochowski, ASTM Spec. Tech. Publ., STP 686, 47 (1978).

302. Erickson, M., M. Alsup, M. Giguere, P. Hyldburg, M. Moseley, D. Whitaker, R. Zweidinger, Techniques for Handling Emulsions, Foaming and Solvent Evaporation in Priority Pollutant Analysis, EPA Contract No. 68-02-2759, 250 p. (1980).

303. Wu, C., I. H. Suffet, Anal. Chem., 49, 231 (1977).

304. Acheson, M. A., R. M. Harrison, R. Perry, R. A. Wellings, Water Research, 10, 207 (1976).

305. Mieure, J. P., J. Amer. Water Works Assoc., 69, 60 (1977).

306. Gough, T. A., K. S. Webb, M. F. McPhail, Talanta, 15, 437 (1977).

307. Fiddler, W., J. W. Pensaben, R. C. Doer, C. J. Dooley, Talanta, 15, 441 (1971).

308. Griest, W. H., Proceedings of International Symposium on Analysis of Hydrocarbons and Halogenated Hydrocarbons in the Aqueous Environment, Toronto, Ontario, May (1978).

309. Deetman, A. A., P. Demeulemeester, Anal. Chim. Acta, 82, 1 (1976).

310. Bahler, D. R., M. E. Rasmusson, H. S. Nakaue, Environ. Sci. Technol., 7, 929 (1973).

311. Moza, P., I. Weisgerber, W. Klein, F. Korte, Environ. Contam. Toxicol., 12, 541 (1974).

312. Selikoff, I. J., Environ. Res., 5, 249 (1972).

313. Shadoff, L. A., R. A. Hummel, L. Lamparski, Bull. Environ. Contam. Toxicol., 18, 478 (1977).

314. Sullivan, J. F., G. J. Atchinson, Bull. Environ. Contam. Toxicol., 17, 121 (1977).

315. Colburn, J. A., B. D. Ripley, A. S. Y. Chau, J. Assoc. Offic. Anal. Chem., 59, 188 (1976).

316. Solomon, J., W. L. Lockhart, J. Assoc. Offic. Anal. Chem., 60, 690 (1977).

317. Dale, W. E., J. W. Miles, F. C. Churchill, J. Assoc. Offic. Anal. Chem., 59, 1088 (1976).

318. Brodtmann, N. V., Bull. Environ. Contam. Toxicol., 15, 33 (1976).

319. Lahav, N., Y. Kahonovitch, Water, Air, Soil Pollut., 3, 253 (1974).

320. Lunde, G., J. Gether, B. Josefsson, Bull. Environ. Contam. Toxicol., 13, 656 (1975).

321. Miles, J. W., W. E. Dale, Environ. Anal. Safety Supp., 3, 100 (1975).

322. Pree, D. J., D. K. R. Stewart, Bull. Environ. Contam. Toxicol., 14, 117 (1975).

323. Suffet, I. H., J. Agr. Food Chem., 21, 288 (1973).

324. Ripler, B. D., R. J. Wilkinson, A. S. Y. Chau, J. Assoc. Offic. Anal. Chem., 57, 1033 (1974).

325. Norris, L. A., M. L. Montgomery, Bull. Environ. Contam. Toxicol., 13, 1 (1975).

326. Miller, W. W., J. S. Wilkins, L. L. Dunham, J. Assoc. Offic. Anal. Chem., 48, 10 (1975).

327. Agemian, H., A. S. Y. Chau, J. Assoc. Offic. Anal. Chem., 60, 1070 (1977).

328. Suffet, I. H., J. Agr. Food Chem., 21, 591 (1973).

329. Agemian, H., A. S. Y. Chau, Analyst, 101, 732 (1976).

330. Khan, S. U., R. Purkayastha, J. Agr. Food Chem., 23, 311 (1975).

331. Moody, R. P., R. Greenhalgh, L. Lockhart, P. Weinberger, Bull. Environ. Contam. Toxicol., 19, 8 (1978).

332. Burnham, A. K., G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec, R. Willis, Anal. Chem., 44, 139 (1972).

333. Clark, B. R., M. R. Guerin, Chemical Characterization and Monitoring Studies of Effluents from Emerging Fossil Fuel Processes NTIS Conf. 761131-1, 10 pp (1976).

334. Thompson, J. F., S. J. Reid, E. J. Kantor, Arch. Environ. Contam. Toxicol., 6, 143 (1977).

335. Parker, B., Amer. Lab., 9, 93 (1975).

336. May, T. W., D. L. Stalling, Anal. Chem., 51, 196 (1979).

337. Erickson, M. D., R. A. Zweidinger, L. C. Michael, E. D. Pellizzari, Environ. Sci. Technol., 12, 927 (1978).

338. Moseman, R. F., H. L. Christ, T. R. Edgerton, M. K. I. Ward, Electron Capture Gas Chromatographic Determination of Kepone Residues in Environmental Samples, EPA-600/J-77-091, U. S. Environmental Protection Agency, 13 p. (1976).

339. Austern, B. M., J. M. Cohen, R. A. Dobbs, Environ. Sci. Technol., 9, 588 (1975).

340. Malcuyande, M., J. Assoc. Offic. Anal. Chem., 61, 1459 (1978).

SECTION 5

FRACTIONATION

Many samples of organic pollutants obtained from water require some form of cleanup or division into simpler fractions before final analysis of the components of interest can be carried out. This fractionation aids in the positive identification of compounds in complex mixtures and also makes it possible to analyze members of only a few compound classes, if desired. Possible fractionation techniques can be generally divided into column and noncolumn techniques.

NONCOLUMN TECHNIQUES

Predominant among the noncolumn techniques is solvent partition, although distillation and thin-layer chromatography are also used.

Solvent Partition

Solvent partition processes depend on the preferential distribution of solute into one of two intermittently contacted but immiscible liquid phases. Solute solubility properties may be altered by controlling the pH of the aqueous phase, the basis for the familiar acid/base wash sequences used to advantage in numerous extraction systems.

In the most common application of solvent partitioning, batch mixing of the biphasic system is accomplished manually with separatory funnels. Although a knowledge of distribution coefficients for specific compounds or classes of compounds can be of practical benefit, the exact partitioning procedure (choice of solvents, number of extractions, amounts of solvents, etc.) has most often been determined empirically. The majority of methods published to date use procedures that divide samples into acidic, basic and neutral fractions. Some information is extant on nonaqueous partitions of neutral water pollutants as a means of further subdivision before ultimate analysis.

Applications

For pollutant mixtures isolated from various water sources, solvent partitioning has been used both as a direct cleanup technique for a specific compound or class of compounds (e.g., phenols) and as a fractionation technique for the general analysis of a wide variety of compound types. Thus, several reports(1-5) on the analysis of phenols contained descriptions of basic fractionation techniques as a means of isolating this class of materials from other, chemically dissimilar compounds. Although aqueous sodium hydroxide has been used by most investigators for isolating all acidic materials (e.g., phenols, carboxylic acids, sulfonic acids), weaker acids, i.e., phenols have on occasion been selectively partitioned by successive washes of bicarbonate (strong acids) and sodium hydroxide (phenols).(2,4) The acidity or basicity of specific materials has been used to advantage for cleanup by controlled pH solvent partitions. For example, a known chemical carcinogen, 4-ethylsulfonylnaphthalene-1-sulfonamide, with mildly acidic properties was successfully analyzed from several complex aqueous mixtures (urine, raw and treated wastewater) by isolation via basic extraction.(6)

Other specific compound types isolated by solvent partition schemes include polynuclear aromatic hydrocarbons (PNAs),(7-9) aliphatic hydrocarbons,(10) pesticides,(11-13) and PCBs.(13,14,15) The high hazard potential of PNA hydrocarbons has led to an increased demand for adequate analytical methodology for these compounds from a variety of sample types. Early work on the distribution coefficients of PNAs in various solvents by Wynder and Hoffman(16) and Haenni et al.(17) has been applied to the analysis of such compounds in waters. Acheson et al.(7) and Dunn(8) obtained PNA enriched fractions from river and seawater through selective partitioning into nitromethane and DMSO. By similar procedures, Selene(9) determined levels of 6 representative PNAs in raw and treated wastewater.

For the analysis of saturated hydrocarbons (C_{15}-C_{30}) from sea water, Iliffe and Calder(10) and Blumer(18) used pH adjustment to selectively remove interfering substances during extraction.

Pesticides in water have received a significant amount of attention in recent years. In the analysis of organophosphorus pesticides from manufacturing wastewaters,(11) a partition sequence was used to separate extracted compounds into solubility groups consisting of water soluble compounds at pH 7, organic bases and neutral, water-insoluble compounds. Carbamates were freed from acidic interferences by base washing (potassium carbonate) in procedures reported by Colburn et al.(12) Most recently, analytical methodology for the EPA priority pollutant pesticides has been reported.(13) Significant GC interferences from municipal wastewaters were removed by partition of the pesticide extracts between hexane and acetonitrile. The same procedure was successfully applied to PCB extracts as well.

Partition processes have been incorporated as an integral part of several general analytical schemes for a wide range of water pollutants. In many of these schemes, solvent separations were achieved using the fundamental procedures of Shriner and Fuson.(19) Nonvolatile organic matter in municipal wastewaters has been separated into weak acids, strong acids, neutrals, bases, and amphoteric substances.(20) More recently, Colgrove and Svec(22) have demonstrated the applicability of a liquid-liquid fractionation procedure to simplify the analysis of complex mixtures. Simple acid/base partitioning has been applied in a general screening procedure for ground water(23) and surface water.(24) General schemes employing solubility separations for industrial wastewaters include work by EPA(25) and Keith.(26) Solvent partition separations can be routinely automated using flow injection technology as reported by Shelly et al.(27) and many others.

Recovery

Recovery data pertaining solely to partition processes are limited in published reports. Muso(1) showed a wide and inconsistent range of recoveries for phenols when base extracted from industrial wastewaters. Eichelberger's procedures for phenols(5) claim overall recovery of 96% for phenol. Radioactive tracers have been used for the determination of recovery of benzo(a)pyrene (BaP) from marine sediments(8) [approximately 90%] and hydrocarbons from sea waters(10) [99%]. Data for the recovery of several carbamate pesticides from natural waters by pH adjusted partition were reported by Colburn(12). Optimum values of 87-98% were reported for six such pesticides. Colgrove and Svec(22) report recoveries for their complex fractionation scheme ranging from 40% to 90% for standard solutions.

Water Types

Partition schemes have been employed in the analysis of ground waters,(23) surface waters,(3,7,8,10,12,24) industrial wastewaters,(1,2,11,25,26) municipal wastewaters,(6,9,13,20,21) and drinking water.(21)

Advantages/Disadvantages

The selectivity of the solvent partition process provides the greatest advantage for its use. Desired components can often be selectively partitioned into a single fraction, well separated from major interferences. In other applications, very complex samples can be simplified by partition mediated fractionation into groups of compounds of similar properties for subsequent analysis, although compounds are sometimes divided between two or more fractions reducing detection limits and complicating data analysis.(22) In some cases, *e.g.*, the separation of acids, grouping is advantageous for derivatization purposes. Compared to other fractionation techniques, such as chromatography on active surfaces, solvent partition represents a very mild procedure that can minimize artifact formation. Recoveries appear to be moderate to good. The equipment required is unsophisticated and inexpensive, and minimal training of laboratory personnel is required for the partitioning process.

Subjecting the sample to solvent partitioning necessarily entails the use of large quantities of solvent. The usual problems attendant to the use of quantities of solvent (solvent removal, emulsion formation, greater sample manipulation) represent disadvantages. In addition, there is the possibility that sample alteration may occur, particularly during acid or base treatment. The literature provides little information regarding this point.

Conclusion

The use of solvent partitioning of complex water samples appears to be widespread. Some form of the technique is embodied in general screening methods that have been proposed to date for phenols,(5) priority pollutant pesticides and PCBs,(13) and priority pollutant organics from sludge.(13) The technique is one of the two most commonly used cleanup or sample fractionation procedures (along with column chromatography).

Distillation

Although distillation is not a commonly used fractionation technique, Leenkeer et al.(28) have reported the use of vacuum rotary evaporation to steam-distill aromatic amines, phenols, and neutral compounds from aliphatic amines in retort water.

COLUMN TECHNIQUES

The complexity of environmental samples places a great strain on the capability of the GC/MS system to separate, identify, and quantify individual components. With conventional packed GC columns, the analysis of such complex mixtures of organic constituents is generally impractical and requires some form of prefractionation in order to reduce the number of components which must be resolved in the final analytical step. Use of selective conventional packed GC columns has been reported by Leenheer et al.(28) to selectively analyze aliphatic C_2 to C_5 monocarboxylic acids, volatile nitriles, alcohols, ketones, and lactones in retort water. Although utilization of capillary columns increases the resolution of the GC/MS system by several orders of magnitude, overlap of specific components still occurs. Even where resolution is not in question, however, the sensitivity of capillaries towards degradation by nonvolatile sample constituents makes removal of these components necessary. Since the derivatization of some environmental constituents may be impaired by the presence of others, some type of sample precleanup is desirable.

Column chromatography has been extensively used to provide the necessary prefractionation of environmental samples. This two-phase separation technique is distinguished from the fraction methods (liquid-liquid partition, thin-layer) by utilization of a stationary phase contained as a packed column bed which is continuously eluted with a liquid mobile phase. The stationary phase may be coated on a solid support or the support itself may function as the stationary phase.

Column chromatography has been employed in two forms, open-column and high performance (HPLC), which differ primarily in the degree of resolution possible and the extent of instrument sophistication required. Open-column chromatography is characterized by the use of stationary phase supports with a particle size range of 75-300 microns. Although the resolution obtained with such large particle supports is inherently low (50-200 theoretical plates/m), the cost of materials and associated equipment is also low. The high permeability of these supports allows adequate flow rates of eluent to be achieved utilizing simple gravity-feed techniques in a vertical column arrangement. Separation times using this method are often relatively slow (hours-days); however, this is offset to some degree by its inexpensive nature which allows a number of columns to be set up and run simultaneously.

High performance liquid chromatography is characterized by the use of support particles in the range 5-75 microns and, in particular, the 5-20 micron range which have been termed microparticulate supports. Because of the relatively slow rate of diffusion for molecular species in liquids compared to the gas phase, the size of the porous suppor is of primary importance in determining the efficiency of mass transport and, consequently, the resolution of the column. Smaller particles, however, also mean lower column permeability, and, thus, higher back-pressures are required in order to produce reasonable mobile phase flow rates. A number of pumping systems have been commercially introduced with high pressure capability (3000-10,000 psi). Although the cost of the HPLC system is high; better elution time, reproducibility (±1%), speed (separations in minutes), and resolution (10,000-30,000 plates/h) are realized factors which are not easily optimized with open-column chromatography. In addition, with the commercial availability of many different types of HPLC detectors (refractive index, ultra-violet absorbance, fluorescence, infra-red, electrochemical, conductance), the technique possesses sufficient capability in reproducibility, resolution, and detection sensitivity to serve as a complementary analytical tool in the quantitation of many environmental constituents not amenable to GC.

Chromatographic Modes

Chromatographic separations *via* column chromatography are divided into four basic modes designated: (1) normal phase, (2) reverse phase, (3) ion-exchange, and (4) gel-permeation (GPC). Each is characterized by the principal separation mechanism involved and the nature of the stationary phase. Although the relative elution order of sample constituents can be predicted from the separation mechanism and component structures, this is seldom straightforward since occurrence of mixed media is not uncommon. The mode chosen for a particular separation problem will depend primarily upon the structures and structural differences in the sample components; however, more than one mode will often provide the separation required. In such cases, the choice may ultimately rest upon such considerations as (1) volatility of the mobile phase (ease of removal), (2) amenability to direct analysis by other methods (GC/MS), and (3) type of separation required (class *vs.* structural *vs.* molecular weight).

Normal Phase--

Liquid-Solid Adsorption--Normal phase chromatography is currently the most common separation mode in general use and is characterized by a polar stationary phase and a relatively nonpolar mobile phase. Where the solid support functions as the stationary phase, the technique is termed adsorption chromatography. Retention and selectivity results from the degree and types of interaction which occur between the polar functional groups of eluting components and the active sites (hydroxyl, Lewis acid, ether) on the surface of the support. These factors are easily controlled by proper adjustment of such mobile phase characteristics as dielectric constant, polarizability, hydrogen bonding, and π-bond interaction. Only a few supports have shown much utility for fractionation of the broad range of organic compounds found in environmental matrices: (1) silica, (2) alumina [acidic, neutral, basic] and (3) Florisil (magnesium silicate).

The general utility of open-column adsorption chromatography as a prefractionation technique in the quantitative gas chromatographic (GC) analysis of organic pollutants in water is evident from the extensive literature available. This is particularly true for the analysis of pesticides where significant effort has been expended in improving specificity and recovery.

The effective separation of a mixture of fifty pesticides into four major fractions was reported by Leone.(29) The procedure utilized a mobile phase gradient of hexane → benzene → 90% for all but Di-syston and Dimethoate. The fractionation was utilized as a cleanup step in the GC analysis of the pesticides in natural waters.

The GC analysis of surface water levels of organochlorine and organophosphorus pesticides using both extraction and silica chromatography in the cleanup procedure was reported by Thompson *et al.*(30) Recoveries were determined for the extraction step and for the combined extraction-chromatography.

A comparison of silica vs. alumina as supports for the cleanup of organochlorine pesticides has recently been reported.(31) The results were applied to the GC/ECD analysis of these pesticides in river, sea, and rain water.

Coburn et al.(32) have reported the application of an alumina column cleanup in the GC/ECD analysis of organochlorine pesticides in surface waters. Recoveries from the adsorption column are not given; however, recoveries for the overall procedure were generally high at levels ranging from 0.008-0.030 μg/L.

Later, et al.(33) report a procedure for the separation of a wide range of compounds using neutral aluminum oxide and silicic acid.

Florisil has also been utilized as an adsorbent in the cleanup of organochlorine pesticide samples obtained from surface waters and treated drinking waters.(34) Subsequent quantitation was carried out via GC/ECD.

Kepone® has received considerable individual treatment in recent methodological developments in the analysis of pesticides. Salch and Lee(35) found Florisil provided adequate cleanup of water samples for the analysis of Kepone by GC/ECD down to 20 ng/L. Recovery of Kepone® from the Florisil column was 100% with ~85% for the overall procedure. The mobile phase in the Florisil fractionation was 5% benzene/10% methanol/hexane. A similar GC/ECD procedure utilizing a Florisil cleanup was reported by Moseman et al.(36,37) and also had an overall recovery of ~85% for Kepone®.

A procedure for the Florisil cleanup of water, sediment, and tissue samples prior to GC analysis for the organophosphorus pesticide fenitrothion has been described.(38) Recoveries were 94-110% down to levels of 0.1 μg/g tissue.

Two authors(39,40) have reported use of silica gel cleanup in the GC/MS analysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).

A similar effort in developing cleanup procedures for water samples is also evident for organic pollutants other than pesticides. In particular, silica(41,42) and Florisil(43,44) have both been utilized in GC/MS analysis of a broad range of organics including PNAs, pesticides, PCBs, phthalates, and organochlorine residues. Sample sources include ground water,(41) municipal sewage,(42) surface and drinking water(43) and industrial and energy effluents.(44)

The use of alumina and Florisil cleanup fractionation methods have also been reported for GC analysis of specific pollutants such as pentafluorophenol in natural and wastewaters,(45) bis(2-chloro)ethers and dichlorobenzenes in finished water,(46) and steroids in surface water.(47)

Low resolution HPLC utilizing 37-75 μm silica has been reported for cleanup of wastewater samples prior to GC/MS analysis for priority pollutants,(13) and for separation of aromatics in water prior to GC analysis.(48)

Bidlingmeyer et al.(49) report the novel use of unbonded silica gel with aqueous eluants to separate organic amines from other compounds.

Liquid-Liquid Partition--Coating of the solid support with a stationary liquid phase is termed liquid-liquid chromatography. Retention and selectivity in this technique are governed primarily by the relative solubilities of sample components in the stationary phase vs. the mobile phase. Here again, a large degree of selectivity is possible since individual compound solubility is the result of a complex mixture of interactions. As with adsorption chromatography, variation of the mobile phase composition is generally the most facile way to control these interactions. Reproducibility of the selectivity and retention of a liquid-liquid chromatographic column requires that the stationary phase coating on the support remain uniform. Unfortunately, the finite mutual solubility of even the most immiscible mobile-stationary phase pairs results in eventual stripping of the stationary phase from the support unless special precautions are taken. The nature of these precautions (constant temperature column environment, saturation of the mobile phase with stationary phase, and precolumns) makes the technique cumbersome. This is particularly true since rigorous control of the mobile phase composition eliminates use of gradient elution. Consequently, the fractionation of a complex mixture with a broad polarity range is not possible. The technique is, therefore, self-limiting and seldom used except as part of a mixed-mechanism separation with gel permeation chromatography (GPC).

Bonded-Phase--Difficulties with liquid stationary phase coatings had led to development of chemically bonded stationary phases. Produced by reaction of appropriately functionalized chloro- and alkoxysilanes with a silica support, these phases are bonded to the surface through the formation of C-Si-O-Si linkages. The resulting phase cannot be stripped away physically and is chemically as stable as the underlying support matrix. Siliceous bonded-phase supports are currently available with a variety of functional groups (phenolic, alkene, aromatic, nitrile, amino and diol). Although the general elution order is still that of normal phase separation (*i.e.*, less polar sample components elute first), each bonded phase possesses a specific selectivity towards structural features of the eluting components (*e.g.*, number, position, and type of polar functional groups). The separation mechanism, which operates to produce observed selectivities, can be adsorption, liquid-liquid partition or a mixture of these depending on the stationary phase, sample components, functional groups and the composition of the mobile phase. The relative selectivities of amino and nitrile bonded-phases and silica have been compared for a number of carbamate pesticides.(50) Due to the expensive nature of these bonded supports, they have been utilized only in HPLC where the maximum benefit from their unique selectivities can be realized.

Application of bonded phase to the HPLC separation of polar organic acids and amines in energy effluents has been reported by Felix and Farrier.(51) Both amino and diol bonded-phase supports were utilized.

Specific utilization of the nitrile bonded-phase in HPLC cleanup of chlorophenols in industrial wastewater was reported(2) as part of an overall capillary GC/MS analysis of these pollutants. Recoveries for the HPLC procedure alone were not specified.

Reverse Phase--

The reverse phase chromatographic mode is characterized by the use of a relatively nonpolar stationary phase eluted with a polar solvent (mobile phase). The most common mobile phases are aqueous mixtures since water is one of the most polar solvents available. The nonpolar stationary phase usually consist of an alkylsilane bonded to a siliceous support. Although the separation mechanism is unclear and probably mixed, retention in this mode appears to depend primarily on the hydrophobicity of sample components rather than any affinity between them and the stationary phase. Thus, the general elution order in this mode is the reverse of that experienced in normal phase chromatography (*i.e.*, the most polar components elute first). As with the bonded-phase supports used in the normal phase separations, the expensive nature of these bonded materials has precluded their use in low resolution open-column chromatography. Although the inexpensive polymeric materials used in accumulator columns work on the same principle, their poor packing and mass transport properties makes then unsuitable for fractionation of sample components.

Reverse phase HPLC applications normally utilize either a C_8- or C_{18}-alkyl bonded phase with a methanol/water or acetonitrile/water eluent. Since polar sample components elute most rapidly, sample losses for polar constituents are often lower for this mode than for normal phase. Unfortunately, use of water in the mobile phase represents a major drawback as the solvent must either be removed by freeze-drying or the sample components re-extracted into an organic solvent for evaporation.

Unlike normal phase, organic components with ionizable functional groups (e.g., carboxyl, amino) can be easily chromatographed in the reverse phase mode. In order to obtain good peak shape (and hence resolution), the ionic equilibrium between neutral and salt forms must be suppressed (ionic suppression) through control of mobile phase pH such that are form predominates. Alternatively, a hydrophilic counter-ion may be added to the mobile phase. Such an ion functions to produce either a more hydrophilic ion-pair with some of the eluting sample components or partitions into the stationary phase to produce a liquid ion-exchange column. The predominating mechanism is dependent primarily on the mobile phase composition. The relative retentions of ionic components are sensitive to mobile phase pH as well as the concentration of the counter-ion.

Most applications of reverse phase HPLC to water analysis involve both major separation of sample components and subsequent quantitation. This is primarily due to three factors: (1) the difficulty in removing the aqueous mobile phase for subsequent GC analysis, (2) the inherent high resolution capability of reverse phase HPLC and (3) the high sensitivity obtained for some organic pollutants using available uv and fluorescence HPLC detectors. In addition, GC problems of derivatization and thermal instability of some pollutant types must also be considered since such difficulties may be eliminated through the use of analytical HPLC.

A broad range of organic water pollutants has been analyzed by reverse phase HPLC methods including alcohols,(52) acids,(52) amines,(52) esters,(52) hydrocarbons,(51,52,53) PNAs,(51,52,54) phenols,(3,52) PCBs,(52,55) pesticides,(3,52) nitrosamines, organosilicones,(51) and phthalates.(57)

Reverse phase HPLC can also be utilized for preconcentration of organics from water in much the same fashion as XAD. An important advantage to the HPLC version is that direct analysis of individual sample components using gradient elution can be accomplished without further sample handling. The utility of trace enrichment in the reverse phase HPLC analysis of organics in water has been discussed by several authors.(58,59)

Only one author has utilized reverse phase HPLC as a cleanup technique for subsequent GC/MS analysis of aqueous organics.(60) The overall analytical procedure was used to evaluate the effect of oxidation on chlorinated PNAs.

Ion Exchange--

As implied by its name, ion exchange chromatography functions through exchange of ions between the mobile phase and ionic functional groups in the stationary phase. By its very nature, this chromatographic mode is applicable only to the separation of ionizable sample constituents. Either acidic or basic sample components may be retained through the proper choice of an anionic (1° amine, quaternary ammonium) or cationic (sulfonic acid, carboxylic acid) stationary phase functional group. For a given stationary phase, the degree of retention and relative selectivity depends primarily upon the relative pKas of the sample components and the pH of the mobile phase. Overall retention can be controlled by changing the mobile phase ionic strength. It is important to point out that the backbone of the ion exchange support may be either polymeric (polystyrene, styrene-divinylbenzene) or siliceous (with ionic functional groups bonded through alkyl or aromatic linkages). For this reason, retention anomalies are frequently experienced for the fractionation of ionic species with considerable lypophilic and/or aromatic character (e.g., fatty acids, phenols).

Ion exchange has had greatest application in the concentration of ionic pollutants from water (accumulator columns). However, through careful control of those factors which affect retention (pH and ionic strength) "ion retardation", as it might well be called, effectively separates ionic species according to relative acidity, or basicity, as well as isolates ionic from neutral species.

Much recent work has been performed using the low resolution open-column form of ion exchange chromatography. Two authors have reported its application in the analysis of organic acids.(61,62) Leenheer et al.(28) report the use of open ion exchange columns to isolate individually aromatic amines, phenols, aromatic carboxylic acids, hydroxypyridines, pyridine-carboxylic acids and aliphatic amines. Junk et al.(12) have also reported the use of open ion exchange columns for the selective fractionation of alcohols, PHAs, halogen compounds, organic acids, and phenols from complex mixtures. Curtis and Rogers(63) reported recently on the optimization of the retention and elution of aromatic amines on XAD-8 resins. The use of this technique in the cleanup fractionation of organic acids in surface water prior to derivatization and GC analysis has also been reported.(64)

The high resolution application of this technique (HPLC) is somewhat more extensive than that of the low resolution counterpart. The former has been reported for the HPLC analysis of amino acids in surface and drinking water;(54) and nucleosides, purines, pyrimidines, aromatic acids and phenols in sewage effluents and cooling water.(65) Jolley et al. have, in addition, reported the separation of a wide range of organics (carbohydrates, polyols, aliphatic and aromatic acids, amino acids, phenols, indoles, pyridines, purines, and pyrimidines) from natural and process waters with identification of many components via GC and GC/MS.(66,67,68) An unusual application of ion exchange was reported by Hannai and Walton(55) in which the reverse phase separation characteristics of the ion exchange support were compared to those of a bonded-alkyl (C_{18}) column.

Gel Permeation--

Gel permeation chromatography (also referred to as GPC, size exclusion or molecular sieve chromatography) differs from other chromatographic modes in that interaction between the eluting sample components and the support surface is undesirable. While complete elimination of such interactions is not always possible, under ideal circumstances the retention and selectivity of this chromatographic mode are derived completely from the ability of molecular species to enter the pores of the support. Hence, retention is controlled solely by the molecular size of the eluting species relative to the size of the pores in the support. It follows, then, that large molecules will elute quickly (lower retention) while smaller molecules are retained in proportion to the time they spend in the stagnant mobile phase pools in the interior of the support. In a polar mobile phase, compounds with polar functional groups are normally surrounded by a cage of closely associated solvent molecules (a hydration sphere for water). Therefore, it should be emphasized that it is the "effective" molecular size in solution which is important rather than the absolute molecular size. Not only does this consideration allow more accurate prediction of elution orders, but it also provides a means of modifying the selectivity of the GPC column for sample components capable of such molecular associations.

There are three major types of GPC supports currently available: (1) rigid siliceous supports, (2) semirigid polymeric supports, and (3) nonrigid carbohydrate-based supports. Although all of these may be utilized in open-column (low resolution) fractionation, only the rigid and semirigid materials are sufficiently stable to withstand the high pressures utilized in HPLC. Aside from selectivity changes, the effect of the mobile phase on the support material must also be considered. Siliceous supports are stable over the entire range of solvent polarities; however, with polar sample components, surface adsorption may become an important factor contributing to retention. Once recognized, this problem can often be dealt with by introduction of a semipolar bonded phase on the support surface or addition of polar modifiers to the mobile phase.

Polymeric supports suffer from problems associated with swelling during solvent changes. If these changes are too extreme or rapid, column collapse (and column plugging) ultimately occurs. Certain solvents may also attack the polymeric structure and cause decomposition. In addition, the alkylaromatic character of polymeric gels makes them hydrophobic and nonwetting aqueous solvents cannot be used. Furthermore, undesirable reverse phase interactions may occur (as with polymeric ion exchange supports).

Nonrigid carbohydrate gels (e.g., Sephadex) are mechanically unstable and therefore require very slow flow rates even under open-column conditions. They cannot be used with organic mobile phaes since they are hydrophilic and will not wet sufficiently. In addition, the polar functional groups (hydroxyl, ether) may produce adsorption interactions if precautions are not taken.

Open-column GPC has been shown to be extremely useful in removing high molecular weight interferences (e.g., humic acids) from water and has been utilized as a sample cleanup procedure in the analysis of pesticides,(69,70) phenols,(69) priority pollutants,(71) Kepone®,(36) and steroids.(47) The most common GPC support utilized is the polymeric type. The GPC technique has also been employed by several authors as a prefractionation method for the GC/MS analysis of priority pollutants.(42,71)

High resolution GPC (HPLC) has not found much use so far in the prefractionation of water samples for GC and GC/MS analysis. Several authors have reported its use in analysis of organosilicones in industrial wastewaters,(56) organophosphorus compounds in natural water,(72) and phthalates in river water(73) by other methods. The technique was, however, utilized by Bean *et al.** in the GC analysis of halogenated organics and PNAs in natural water with ECD, FID, and MS detection.

REFERENCES

1. Mousa, J. J., Symposium on Measurement of Organic Pollutants in Water and Wastewaters, ASTM Committee D-19 on Water, Denver, CO, June, 1978.
2. Lindström, K. J. Norton, J. Chromatogr., 128, 13 (1976).
3. Wolkoff, A. W., R. H. Morose, J. Chromatogr., 99, 731 (1974).
4. Kleverlaan, N. T. M., Chem. Weekbl., 71, 13 (1975).
5. Eichelberger, J., W. Dressman, J. Longbottom, Environ. Sci. Technol., 4, 576 (1970).
6. King, J. R., M. C. Bowman, Biomed. Med., 12, 313 (1975).
7. Acheson, M. A., R. M. Harrison, R. Perry, R. A. Wellings, Water Res., 10, 207 (1976).
8. Dunn, B. P., Environ. Sci. Technol., 10, 1018 (1976).
9. Saxena, J., D. Basee, J. Kozuchowski, Method Development and Monitoring of PNA Hydrocarbons in Select U. S. Waters, EPA-R-803977, July, 1977.
10. Iliffe, T. M., J. A. Calder, Deep Sea Research, 21, 481 (1974).
11. Spigarelli, J., Org. Compounds in Organophosphorus Pesticide Manufacturing Wastewaters, Final Report, EPA Contract No. 68-03-2343 (1977).
12. Coburn, J. A., B. D. Ripley, A. S. Chau, J. Assoc. Offic. Anal. Chem., 59, 862 (1976).
13. Proposed Protocol for EPA Priority Pollutants, August, 1978.
14. Oliver, G. B., K. D. Bothen, Anal. Chem., 52, 2066 (1980).
15. Millar, J. D., R. E. Thomas, H. J. Schattenberg, III, Anal. Chem., 53, 214 (1981).
16. Hoffmann, D., E. L. Wynder, Anal. Chem., 32, 295 (1960).

17. Haenni, E. O., J. W. Howard, F. L. Joe, J. Assoc. Offic. Anal. Chem., 45, 67 (1962).

18. Blumer, M., Organic Matter in Natural Waters, D. W. Hood, ed., University of Alaska, 1970, pp. 153.

19. Shriner, A. L., R. C. Fuson, Systematic Identification of Organic Compounds, 2nd Ed., John Wiley & Sons, New York, (1940), 252 pp.

20. Aldrich, M. H., T. A. Pressley, C. Chapman, Welebira, WRRC Report No. 9, Characterization of Non-Volatile Organic Material during Physical-Chemical Treatment of the District of Columbia Raw Wastewater, Water Resources Research Center, 1976.

21. Lin, D. C. K., D. A. Contos, R. L. Foltz, V. R. Goff, T. L. Hayes, P. P. Kelly, D. A. Lucas, B. S. Mackey, B. A. Petersen, L. E. Slivon, R. Warren, S. C. Watson, GC/MS Analysis of Organics in Drinking Water Concentrates and Advanced Waste Treatment Concentrates, Lake Tahoe II, Pentane Concentrate Analysis Report, Vol. 1, U. S. Environmental Protection Agency, Project No. 68-03-2548 (1978).

22. Colgrove, S. G., H. J. Svec, Anal. Chem., 53, 1737 (1981).

23. Keith, L. H., Identification and Analysis of Organic Pollutants in Water, Chapter 27, Ann Arbor Science, Ann Arbor, MI, (1976), 453 pp.

24. Ewing, B. B., E. S. K. Chian, J. C. Cook, C. A. Evars, P. K. Hopke, E. G. Perkins, Monitoring to Detect Previously Unrecognized Pollutants, Progress Report No. 2, EPA Contract No. 68-01-3234, 1976.

25. Solubility Separation by pH Adjustment: A Procedure for the Extraction of Industrial Organic Chemicals in Effluents and Streams, U. S. Environmental Protection Agency WO-1/75.

26. Keith, L. H., Environ. Sci. Technol., 10, 555 (1976).

27. Shelly, D. C., T. M. Rossi, I. M. Warner, Anal. Chem., 54, 87 (1982).

28. Leenheer, J. A., T. I. Hoyes, H. A. Stuber, personal communication.

29. Leoni, V., J. Chromatogr., 62, 63 (1971).

30. Thompson, J. F., S. J. Reid, E. J. Kantor, Arch. Environ. Contam. Toxicol., 6, 143 (1977).

31. Wells, D. E., S. J. Johnstone, J. Chromatogr., 140, 17 (1977).

32. Coburn, J. A., I. A. Valdmanis, A. S. Y. Chau, J. Assoc. Offic. Anal. Chem., 60(1), 224 (1977).

33. Later, D. W., M. L. Lee, K. D. Bartle, R. C. Kong, D. L. Vassilaros, Anal. Chem., 53, 1612 (1981).

34. Smillie, R. D., A. A. Nicholson, O. Meresy, W. K. Duholke, G. A. V. Rees, K. Roberts, C. Fung, Organics in Ontario Drinking Waters, Part II, A Survey of Selected Water Treatment Plants, Ontario Ministry of the Environment-OTC7703-Project No. AAN-7504, April (1977).

35. Saleh, F. Y., G. F. Lee, Environ. Sci. Technol., 12(13), 297 (1978).

36. Moseman, R. F., H. L. Crist, T. R. Edgerton, M. K. Ward, Electron Capture GC Determination of Kepone Residues in Environmental Samples, U. S. Department of Commerce, NTIS PB-278-594, 219 pp., November (1976).

37. Moseman, R. F., H. L. Crist, T. R. Edgerton, M. K. Ward, Arch. Environ. Contam. Toxicol., 6, 221 (1977).

38. Grift, N., W. L. Lockhard, J. Assoc. Offic. Anal. Chem., 57(6), 1282 (1974).

39. L. A. Shadoff, R. A. Hummel, L. Lamparski, Bull. Environ. Contam. Toxicol., 18(4), 478 (1977).

40. Ramstad, J., N. H. Mahle, R. Mataton, Anal. Chem., 49, 386 (1977).

41. Robertson, J. M., C. R. Toussaint, M. A. Jorque, Organic Compounds Entering Ground Water from a Landfill, U. S. Environmental Protection Agency, EPA-660/2-74-077, 47 pp., September (1974).

42. Warner, J. S., G. A. Jungclaus, T. M. Engel, R. M. Riggin, C. C. Chuang, Proposed Protocol for Priority Pollutants, U. S. Environmental Protection Agency, August (1978).

43. Keith, L. H., A. W. Garrison, F. R. Allen, M. H. Carter, T. L. Floyd, J. D. Pope, A. D. Thurston, Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, p. 329 (1976).

44. Clark, B. R., M. R. Guerin, Chemical Characterization and Monitoring Studies of Effluents from Emerging Fossil Fuel Processes, Oak Ridge National Laboratory, NITS CONF-761131-1.

45. Chau, A. S., J. A. Coburn, J. Assoc. Offic. Anal. Chem., 57(2), 389 (1974).

46. Dressman, R. C., J. Fair, E. F. McFarren, Environ. Sci. Technol., 11(7), 719 (1977).

47. Okuno, I., W. Higgens, Bull. Environ. Contam. Toxicol., 18, 428 (1977).

48. Welebir, A., W. M. d'Angelo, S. W. Bigelow, M. H. Aldridge, Evaluation of High Performance Liquid Chromatography Packings for the Concentration and Separation of Organic Materials in Water, Naval Research Laboratory, NOO 173-76-C-0182, 39 pp., November (1977).

49. Bidlingmeyer, B. A., J. K. Del Rios, J. Korpi, Anal. Chem., 54, 442 (1982).

50. Sparacino, C. M., J. W. Hines, J. Chromatogr. Sci., 14, 549 (1976).

51. Felix, W. D., D. S. Farrier, R. E. Poulson, High Performance Liquid Chromatographic Characterization of Oil-Shale Retort Waters, Battelle Pacific Northwest Labs., NTIS BNWL-SA-6052, 7 pp., April (1977).

52. Veith, G. D., N. M. Austin, Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science Publ., Inc., Ann Arbor, MI, p. 297 (1976).

53. May, W. E., S. N. Chesler, S. P. Cram, G. H. Gump, H. S. Hertz, D. P. Enagonio, S. M. Dyszel, J. Chromatogr. Sci., 13, 535 (1975).

54. Kasiske, D., K. D. Klinkmuller, M. Sonneborn, J. Chromatogr., 149, 703 (1978).

55. Hanai, T., H. F. Walton, Anal. Chem., 49(6), 764 (1977).

56. Cassidy, R. M., M. T. Hurteau, J. P. Mislan, R. W. Ashley, J. Chromatogr. Sci., 14, 444 (1976).

57. Otsuki, A., J. Chromatogr., 133, 402 (1977).

58. Frei, R. W., Intern. J. Environ. Anal. Chem., 5, 143 (1978).

59. Creed, C. G., Research/Development, September, 40 (1976).

60. Carlson, R. M., R. Caple, A. R. Oyler, Water Chlorination, R. L. Jolley, H. Gorchev, D. H. Hamilton, eds., Ann Arbor Science, Inc., Ann Arbor, MI, p. 59 (1978).

61. Kabeya, H., K. Uytaka, Nippon Kugaku Kaishi, 11, 1910 (1975).

62. Horikawa, K., Japan Anal., 21, 806 (1972).

63. Curtis, M. A., L. B. Rogers, Anal. Chem., 53, 2347 (1981).

64. Lasson, R. A., J. C. Weston, S. M. Howell, J. Chromatog., 111, 43 (1975).

65. Jolley, R. L., G. Jones, W. W. Pitt, J. C. Thompson, Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, Ann Arbor, MI, p. 233 (1976).

66. Jolley, R. L., S. Katz, J. E. Mrochek, W. W. Pitt, W. T. Rainey, Chemtech., May, 312 (1975).

67. Jolley, R. L., W. W. Pitt, C. D. Scott, G. Jones, J. E. Thompson, Trace Substances Environ. Health, 9, 247 (1975).

68. Jolley, R. L., W. W. Pitt, J. E. Thompson, 1977 Environmental Technology, 23rd Annual Technical Meeting of the Institute of Environmental Sciences, Los Angeles, CA, April (1977).

69. Stalling, D. L., L. M. Smith, J. D. Petty, Symposium on Measurement of Organic Pollutants in Water and Wastewater, ASTM Committee D-19 on Water, Denver, CO, June (1978).

70. Burchfield, H. P., E. E. Storrs, J. Chromatogr. Sci., 13, 202 (1975).

71. Kleopfer, R. D., W. W. Bunn, Proposed Protocol for Priority Pollutants U. S. Environmental Protection Agency, August (1978).

72. Misear, R. A., Investigation of the Chemical Identity of Soluble Organophosphorus Compounds Found in Natural Waters, Tennessee Water Resources Research Center, Res. Rtp. No. 64, April (1978).

73. Mori, J., J. Chromatogr., 129, 53 (1976).

SECTION 6

CHEMICAL DERIVATIZATION

Derivatization is the modification of chemical compounds and is often used to eliminate problems in qualitative and quantitative analysis. For organic compounds, derivatization involves the replacement of an active hydrogen or a polar functional group with a less reactive constituent. This effectively reduces compound polarity and decreases the possibilities of hydrogen bonding to give increased volatility as well as chemical stability. For gas chromatography, derivatization minimizes solute-sorbent interaction resulting in reduced irreversible adsorptive losses, reduced peak tailing, and improved compound separation.

Since chemical derivatization is an additional step in a procedure, it is a potential source of error which could seriously affect the quantitative precision and accuracy of an analytical scheme. For this reason, a thorough knowledge of the reactions used and the factors which influence the results is necessary. Ideally, all derivatization reactions should be efficient, quantitative, reproducible, rapid, and easy to perform and should produce a stable, volatile derivative which is free from contaminants and other experimental artifacts. Unfortunately, no reaction satisfies all these requirements, and existing methodologies are compromises which satisfy the most important criteria for a given experiment.

The purpose of this review is to survey available analytical techniques in order to determine which methods are most suited for the comprehensive, nonselective analysis of organic compounds in a variety of water matrices. When considering chemical derivatization in this light, it is necessary to know: (a) the compounds to be derivatized; (b) the existing methodologies; (c) the yields and recoveries of derivatized compounds; (d) the advantages and limitations of these procedures; and (e) the effect of sample matrix on the derivatization technique.

In addressing these questions, derivatization reactions will be discussed first, by considering the most commonly used techniques and, second, by considering compound classes most often derivatized. Specific attention will be given to references pertinent to environmental analysis.

DERIVATIZATION METHODS

It is advantageous to consider the most common derivatization techniques before discussing modification of different compound classes. In this way, inherent advantages and disadvantages should be apparent when comparing the suitability of various techniques for specific polar functional groups.

Derivatization procedures may be divided into six classes: esterification, acylation, silylation, ether formation, cyclization, and reaction with dialkyl acetals. Each type of reaction including methodology, product isolation, benefits, and limitations will be discussed.

Esterification

Esterification of carboxylic acids increases volatility and protects polar acid groups during subsequent reaction. Methyl esters are the most widely used. Higher alkyl esters have also been employed both to provide a less volatile derivative and to distinguish derivatives from naturally occurring methyl esters in environmental samples. For simplicity, only methylating reactions will be discussed. However, the preparation of other alkyl esters is essentially equivalent using higher homologues of the derivatizing agent.

Methylation with diazomethane is the most common esterification technique. Diazomethane is gradually added to an ethereal solution of the acidic compounds until esterification is complete. Reagent is either added as an organic solution(2) or is bubbled through the reaction medium(2,3) as a vapor. This latter method is somewhat safer, and also introduces fewer reagent contaminants. Anhydrous conditions are recommended to prevent diazomethane from reacting with water.(4)

Diazomethane esterifications are simple, rapid, and, for the most part, quantitative. The major disadvantages to this reagent are that it is toxic, explosive, and highly reactive. Polymer formation may occur during prolonged exposure and, since the reagent is not removed after esterification, best results are achieved when analysis immediately follows derivatization.

Problems associated with high blanks have been reported by several investigators.(5,6) Excess reagent may be simply evaporated.

Methanol with an appropriate catalyst may be used as an esterification reagent. In the case of a strong acid catalyst (e.g., HCl or H_2SO_4), a methanolic solution of the sample is refluxed on a water bath.(7) The reagents for this reaction are safe, readily available, and introduce minimal contamination. However, applying heat to a strongly acid solution may produce reactions with other functional groups or sample components. Boron trifluoride in methanol is a particularly good reagent for esterifying polyfunctional carboxylic acids.(8) Unlike the Fisher esterification, where a strongly acidic environment prevails, this reaction proceeds under mild conditions. It effectively esterifies the carboxy group without affecting most other substituents in the molecule or the stability of the acid itself. With both methanolic procedures, it is easy to remove extraction products from the esterification media using a water/organic solvent extraction procedure. The possibilities of artifact formation and sample contamination are reduced under these conditions. Unfortunately, these reagents often cause side reactions such as dehydration and isomerization of polyfunctional compounds. Transesterifications have also been reported. These disadvantages limit the use and applicability of the above methylating reagents.

Methylation of aliphatic and aromatic carboxylic acids by pyrolysis of their quaternary ammonium salts is a common esterification procedure. Derivatization is carried out in conjunction with gas chromatography by allowing the reaction to occur in a heated precolumn reactor or on the GC column itself. Pyrolytic methylation has been described for a number of aromatic and aliphatic carboxylic acids. Reaction is achieved by dissolving the carboxylc acid(9) in methanol, titrating to the phenolphthalein end point with tetramethylammonium hydroxide, and injecting 1 to 5 μL of this solution directly into the gas chromatograph.(7)

The major advantage to this technique is its inherent simplicity. Quantitative yields with high reproducibility have been claimed for several long chain fatty acids.(10) Unfortunately, the alkalinity of the reagent combined with high reaction temperatures can cause isomerization and degradation of polyunsaturated acids.(11)

This reaction and other pyrolytic techniques do not appear to be well-suited to a comprehensive scheme for organic analysis. As already stated, compound degradation could cause significant problems. Reaction conditions cannot be well-controlled, and, therefore, no adjustments can be made for differences in compound reactivity. Finally, introducing large volumes of derivatizing agent into the ion source of a mass spectrometer (MS) may cause significant problems when MS is used as the detection system.

Other esterification reagents include dimethylsulfate(12) and 2,2-dimethoxypropane.(4) Neither of these reagents has been used extensively in environmental analysis.

A number of studies have compared the efficiency of various methylating agents for the esterification of herbicidal acid groups. In all cases, diazomethane gave highest yields. BF_3-catalyzed methanol was effective except for hindered functional groups, whereas proton catalyzed reaction gave lowest yield.(13) Scoggins and Fitzgerald(14) showed that dimethyl sulfate in methanol is as efficient a methylating reagent as diazomethane for the chlorophenoxyacetic acid herbicides. The ability to give consistently high yields without interfering side reactions has made diazomethane the reagent of choice for esterification reactions.

Silylation

Silylation is the introduction of a silicon-containing group into an organic molecule usually in substitution for an active hydrogen. Trimethylsilyl (TMS) derivatives are the most common modifiers having the chemical structure $Si(CH_3)_3$. Preparation of possible silyl derivatives is represented by the scheme(4)

$$\begin{array}{lcl}
\mathrm{-OH} & & \mathrm{-O-Si(CH_3)_3} \\
\mathrm{-COOH} & & \mathrm{-COO-Si(CH_3)_3} \\
\mathrm{-SH} & \xrightarrow[\text{donor}]{\text{TMS}} & \mathrm{-S-Si(CH_3)_3} \\
\mathrm{-NH_2} & & \mathrm{-NHSi(CH_3)_3} \\
>\mathrm{NH} & & \mathrm{=N-Si(CH_3)_3}
\end{array}$$

and if the enolized carbonyl group is included, then all the common polar groups are represented. The general order for decreasing ease of reaction is: alcohols (primary, secondary, then tertiary), phenols, carboxylic acids, amines (primary, secondary, then tertiary), and amides.

Conditions necessary for TMS derivatization have been studied extensively and, for the most part, are well understood.(15) For high derivative yield, a reaction scheme must provide: (a) a derivatizing agent which is more basic than the compound to be derivatized; (b) a polar reagent solvent capable of stabilizing the charged reaction intermediate; and (c) a mechanism for removing spent reagents and hydrogen ions as the reaction proceeds. A variety of reagents, catalysts, and reaction conditions have been employed to meet the above specifications. Commonly used reagents, their chemical structures and reaction products are given in Table 1. Reagents are listed in order of decreasing reactivity.(15)

Since most TMS reagents are more volatile than their associated derivatives, they should not interfere with chromatographic analysis, and in most cases, no attempt is made to separate the reaction products from the reaction mixture.(16) However, during mass spectrometry, reagents often decompose in the ion source to form SiO_2 causing problems such as tailing, baseline drift, and variable sensitivity. In these cases, it may be preferable to isolate derivatives from the reaction mixture via distillation. For the most stable derivatives, low molecular weight alcohols are sometimes added to the reaction mixture to quench unreacted agents and prevent by-product formation.

The main advantages of TMS derivatives are their facile preparation and their ability to modify a variety of functional groups. In addition, they give characteristic mass spectral fragmentation patterns useful for compound identification.(15)

Silylation is often considered an unfailing means of improving GC separations; however, no technique is without limitations. Trimethylsilyl derivatives are unstable in water, requiring that anhydrous conditions be maintained throughout the entire analytical procedure.(17) Carboxylic acid derivatives are the least stable with even the slightest trace of water inducing hydrolysis. Hume(18) discussed the elaborate precautions which must be taken to avoid decomposition of TMS-nitrilotriacetic acid during GC analysis. Derivatives formed from secondary and tertiary functional groups tend to be more stable, suggesting that steric hindrence may prevent hydrolysis.

Table 1. COMMON TMS DONORS

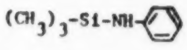
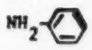
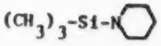
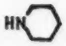
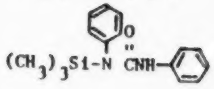
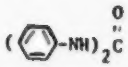
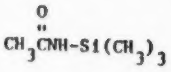
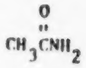
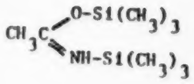
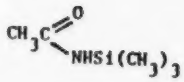
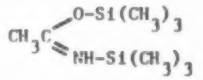
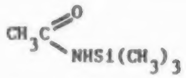
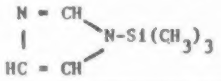
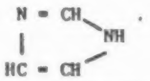
Donor Mixture	Chemical Structure	Reaction Products
1) N-TMS-butylamine	$C_4H_9NSi(CH_3)_3$	C_4H_9NH
2) Trimethylchlorosilane (TMCS)	$Cl-Si(CH_3)_3$	$-Cl^- + H$
3) Hexamethyldisilazane (HMDS)	$(CH_3)_3Si-NH-Si(CH_3)_3$	NH_3
4) Hexamethyldisilazane + pyridine	$(CH_3)_3Si-NH-Si(CH_3)_3$	NH_3
5) Trimethylchlorosilane + pyridine	$Cl-Si(CH_3)$	Cl^-
6) Trimethylchlorosilane + triethylamine	$Cl-Si(CH_3)$	$Cl^-(C_2H_5)_3NH^+$
7) Hexamethyldisilazane + trimethylchlorosilane + catalyst	$(CH_3)_3Si-NH-Si(CH_3)_3$	NH_3
8) Hexamethyldisilazane + ammonium sulfate	$(CH_3)_3Si-NH-Si(CH_3)_3$	NH_3
9) Hexamethyldisilazane + trimethylchlorosilane + pyridine	$(CH_3)_3Si-NH-Si(CH_3)_3$	NH_3
10) N-TMS-aniline		
11) N-TMS-piperidine		
12) N-TMS-diethylamine (TMSDEA)	$(CH_3)_3SiN(C_2H_5)_2$	$(C_2H_5)_2NH$
13) N-TMS-N,N'-diphenylurea		
14) N-TMS-acetamide (MSA)	 $CH_3\overset{O}{C}NH-Si(CH_3)_3$	 $CH_3\overset{O}{C}NH_2$
15) N,O-Bis(TMS)-acetamide (BSTFA)		
16) N-TMS-diethylamine + catalyst	$(C_2H_5)_2N-Si(CH_3)_3$	$(C_2H_5)_2NH$

Table 1 (cont'd)

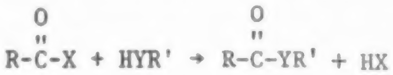
Donor Mixture	Chemical Structure	Reaction Products
17) N,O-Bis(TMS)-acetamide + trimethylchlorosilane		
18) N-TMS-imidazole (TSIM)		

t-Butyl silyl reagents(19,20) have been developed which form sterically hindered products that are relatively stable towards water. These reagents allow silylation to occur even when water is present in the reaction mixture.(21)

Silylated compounds can cause some problems during chromatography. When using a flame ionization detector, silicon dioxide may be deposited on the electrodes which can alter detector response and lead to reduce sensitivity. Ghost peaks have been reported during gas chromatography of silylated phenols.(5) Finally, it should be mentioned that the reactivity of different functional groups toward silylation varies widely. Because of this, reaction time and conditions must be carefully controlled in order to achieve quantitative yields without producing side reactions or degradation products.

Acylation

Acylation is a common derivatization technique for hydroxy, thiol, and amino compounds which unlike silylation can modify even the unreactive tertiary amino group. The chemistry of acylation usually involves the introduction of an acetyl group into the molecule by substitution for a replaceable hydrogen. The reaction proceeds according to the scheme:



$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}X + HYR' \rightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}YR' + HX$$

The reagents most commonly used include: acid anhydrides, acid chlorides, and some substituted derivatives, such as acylated imidazoles, amides, and phenols.(22)

Acyl halides are highly reactive and capable of derivatizing any of the specified functional groups including amides and sterically hindered moieties. Unfortunately, hydrogen halides are produced during derivatization necessitating the presence of a base in the reaction mixture in order to drive the reaction to completion. Excess reagent and HX salts can cause chromatographic problems. However, removal is difficult, somewhat limiting the applicability of this approach.

Acid anhydrides are usually easier to remove at the end of a reaction. Derivatization yields a clean product since only the acylated product and organic acid are formed. However, anhydrides are less volatile than the corresponding halides and may interfere with the chromatography of more volatile products. In addition, the acidic medium makes this reagent unsuitable for acid-sensitive compounds.

Acylation reagents that form basic leaving groups, i.e., acylated imidazoles and acetamides, are more satisfactory for derivatizing acid-sensitive molecules.(23) The basic leaving group associates with the displaced hydrogen to form a neutral by-product. For this group of derivatives, as well as the other reagents, the type and amount of solvent frequently has a significant influence on reaction yield.(24)

Because of their high reactivity, excess reagents may have an adverse effect on subsequent analysis, and, therefore, should be removed.(22) Common problems include: irreversible alterations of the chromatographic column, corrosion or other damage within the chromatographic or GC/MS system, and rederivatization of nonvolatile residues at the top of the GC column. Since the acid anhydrides are the easiest to remove and do not require basic acceptor molecules (like the acid halides), they have become the most common derivatizing reagent.

Halogenated acyl derivatives are commonly used in trace organic analysis.(25) Most polyhalogenated reagents are either acid anhydrides or chlorides which reactions, advantages, and disadvantages parallel those described above. Fluorinated derivatives are the most widely used due to their increased volatility and high electron capture detector (ecd) sensitivity.(22) Some of the most common reagents of this type contain the trifluoroacetyl (TFA), heptafluorobutyl (HFB), pentafluoropropionyl (PFP), and pentafluorobenzyl (PFB) moieties.(26) Two TFA-amide reagents have been developed which form basic amide leaving groups.(22) These reagents produce reaction by-products which are very volatile and easily removed. They also react under mild, nonacidic conditions. Unfortunately, excess reagent is not easily removed and, thus, chromatographic problems may prevail.

Acylated derivatives for both hydroxy and amino groups are easily prepared, and acylation reactions give higher yields than the various methylating procedures. For this reason, acylation is the method of choice for both functional groups.

Ether Formation

Ether derivatives are prepared to protect hydroxy groups but have not been used extensively for GC analysis except in special cases. A number of polyhalogenated ether derivatives have been developed for trace analysis using electron capture detection which, due to its enhanced sensitivity, has been widely used for pesticide residue analysis.

The methods outlined for esterification are also applicable to ether formation. However, since the hydroxy group is less reactive than the carboxy group, yields are usually lower and stronger reaction conditions are required. Khan(24) reported 50-80% yields for the preparation of methyl ethers using diazomethane. High concentrations of the derivatizing agent were needed for good yields.

A base-catalyzed methylation using sodium hydride/methyl iodine/dimethyl sulfoxide(28) was reported for derivatizing various pesticides. Both hydroxy and amino groups were methylated with 60-90% conversion.

Extractive alkylation is a relatively new method for ether formation.(29) Briefly, an organic substrate is extracted as an ion pair (usually as the quaternary ammonium salt) from an aqueous into a nonpolar phase. The poor solvating ability of the organic phase makes the substrate highly reactive towards nucleophilic displacement. In the presense of an appropriate alkylating reagent, reaction occurs rapidly. Pentafluorobenzyl bromide (PFBB) and methyl iodide are two commonly used reagents. The reaction sequence is described by the following equations:

$$I^- + RO^+ \rightarrow IRO^\pm$$

$$IRO^\pm + R'X \rightarrow R'OR + IX^\pm$$

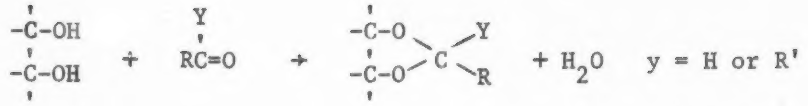
Reaction conditions are mild, fast, and simple. Phenols, carboxylic acids, amines, and amides have been successfully alkylated using this procedure.

Cyclization

Cyclization refers to the reaction of a derivatizing agent with an organic substrate to form a cyclic molecule. For this to occur the substrate must have two functional groups of suitable reactivity with a spatial separation conducive to ring formation. Cyclization reactions avoid multistep procedures such as the acylation-esterification reactions commonly used for amino acid analyses and may also prevent isomerizaton reactions from occurring, thereby simplifying both quantitative and qualitative analysis. Acetals and ketals, siliconides, and boronates are the most common cyclizing derivatives.

Acetals and Ketals--

Cyclic acetals and ketals are normally prepared from diols, triols, and polyhydroxy compounds via interaction with an aldehyde or ketone to form (usually) a dioxolane ring. The derivatization proceeds according to the reaction:



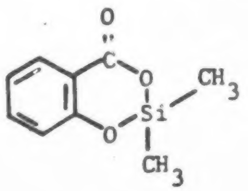
$$\begin{matrix} -\overset{|}{C}-OH \\ -\underset{|}{C}-OH \end{matrix} + \overset{Y}{\overset{|}{RC}}=O \rightarrow \begin{matrix} -\overset{|}{C}-O \\ -\underset{|}{C}-O \end{matrix}\!\!>C<\begin{matrix} Y \\ R \end{matrix} + H_2O \quad y = H \text{ or } R'$$

During derivatization, the carboxyl reagent and organic substrate are dissolved in a suitable solvent (*i.e.*, benzene, *p*-dioxane, or N,N-dimethylformamide) and reacted in the presence of a catalyst.(30) Activation using HCl, H_2SO_4, ethane sulfonic acid, zinc chloride, or anion exchange columns in the H^+ form have given good product conversion. Water formed during the reaction may be removed either using a dehydrating agent such as Na_2SO_4 or azeotropic distillation. Sugars, diols, triols, carbohydrates, sterols, and lipids have all been derivatized successfully using this general procedure.

Acetals and ketals are stable under oxidizing and reducing conditions, and are unreactive towards Lewis (*e.g.*, acetals/ketals undergo several different reactions in the presence of a Lewia acid catalyst) bases. This general property of chemical inertness makes them particularly attractive when multistep derivatization procedures must be employed. As would be expected, these derivatives can undergo hydrolysis. Since reagents are generally low molecular weight carbonyl compounds and the reaction products are limited to the acetals or ketals and water, problems for chromatographic analysis should be minimal. Starting reagents may be removed by distillation if desired.

Siliconides--

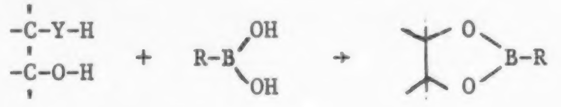
Siliconides are cyclic silyl derivatives formed when a single silicon ion has replaced two reactive hydrogens from a polyfunctional organic substrate. For illustration, the dimethylsiliconide of salicylic acid is shown below.



Successful derivatization using dimethyldiacetoxysilane (DMDAS) in the presence of triethylamine, and dichlorodimethylsilane (DCDMS) in pyridine have been reported.(30) The preparation, advantages, and limitations of these derivatives are the same as those for other silylated products.

Boronates--

Cyclic boronates are five or six member ring heterocyclic compounds formed by the reaction of a substituted boronic acid with a difunctional organic substrate. Boronic acids appear to react with most α- and β-difunctional compounds including diols, enolizable acetals, hydroxy acids, and hydroxylamines according to the generalized reaction scheme:



y = N or O

Derivatizations are rapid and simple. Reaction involves mixing the acid with the substrate at a 1:1 molar ratio in an organic solvent such as acetone, chloroform, DMF or THF. Most reactions are complete within 15 minutes at room temperature. Hydroxyl amines and some sugars require stronger conditions, while α-amino acids will not react at all.(32) Water should be removed to drive the reaction to completion. Butyl, methyl, and phenyl boronates are the most common derivatives--the methyl homolog is usually preferred due to its increased volatility.

Boronate derivatives are stable in air but rapidly hydrolyze in water, moist organic solvents, and weak acids. Because they give quantitative yields when reacted with substrate on an equimolar basis, only solvent and derivatized products are generally present at the end of the reaction eliminating the necessity for any isolation or cleanup procedures and minimizing many chromatographic problems. A nonlinear GC response has been reported on OV-17 columns at the 1 μg level.(33) Carbohydrates, catecholamines, corticosteroids, hydroxy fatty acids, monoglycerides, and prostaglandins have all been analyzed as boronate derivatives.(31)

Reactions with Dialkyl Acetals

Dimethylformamide diacetals react with a variety of functional groups to form derivatives suitable for gas chromatography. Some examples are depicted in Figure 15.(8) As illustrated, carboxylic acids, phenols, amides, and thiols react to give the corresponding alkyl derivatives although N-dialkyl amino formation occurs for the free amine. Amino acids react to give fully derivatized products. Sterically hindered acids, *i.e.*, trimethyl-

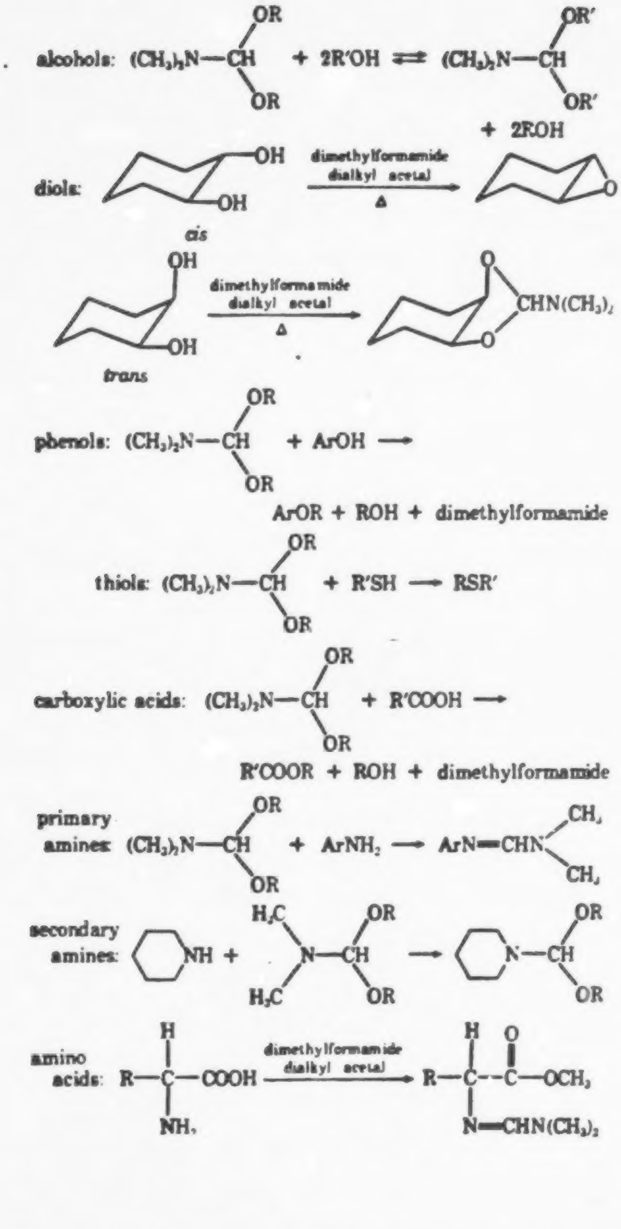

alcohols: (CH3)2N—CH(OR)2 + 2R'OH ⇌ (CH3)2N—CH(OR')2 + 2ROH
diols:
dimethylformamide dialkyl acetal
Δ
cis
trans
CHN(CH3)2
phenols: (CH3)2N—CH(OR)2 + ArOH →
ArOR + ROH + dimethylformamide
thiols: (CH3)2N—CH(OR)2 + R'SH → RSR'
carboxylic acids: (CH3)2N—CH(OR)2 + R'COOH →
R'COOR + ROH + dimethylformamide
primary amines: (CH3)2N—CH(OR)2 + ArNH2 → ArN═CHN(CH3)2
secondary amines:
amino acids:
R—C(H)(NH2)—COOH
R—C(H)(N═CHN(CH3)2)—C(O)—OCH3

Figure 15. Dialkyl acetal derivatization reactions.

benzoic acids, react almost as rapidly as unhindered acids. Other sterically hindered functional groups should react in the same way.

Derivatizations are performed by dissolving the organic substrate and excess of reagent in almost any organic solvent and heating the mixture at 50° to 60°C for 15 minutes. The reaction is usually complete when the substrate has been dissolved and heating is utilized only to facilitate dissolution. Since N,N-dimethylformamide acetals are moisture sensitive, the derivatization should be performed under strictly anhydrous conditions to prevent side reactions from occurring.(34) It has been shown that a number of extraneous products are formed during the chromatographic analyses of this reagent. To avoid this problem, excess reagent is removed by distillation and the sample is purified using a solvent:water extraction procedure. Under these conditions, quantitative recoveries with no interferences should be obtained.

This technique appears attractive since it is rapid, simple, and non-selective. Unfortunately, it has not been used in environmental analysis, and, therefore, no direct assessment of applicability can be made.

COMPOUND CLASS REACTIONS

The purpose of this section is to report and compare analytical methodologies used to derivatize specific compounds within a given class. When available, both yield and recovery data will be given. Greatest emphasis has been given to references reporting on the analysis of environmental samples.

Alcohols and Phenols

Since most lower alcohols do not present a problem for GC analysis and since environmental samples are a complex mixture of compounds difficult to derivatize quantitatively, the practice of chemically modifying monohydroxy alcohols is not common. In contrast, the derivatization of phenols and substituted phenols has been studied by many investigators and is practiced extensively.

Trimethylsilyl derivatives of phenolic contaminants in aqueous environmental samples are frequently prepared to improve their chromatographic properties. Both Cooper(35) and Murray(36) analyzed and quantified phenolics in aqueous samples. Ewing(5) prepared silyl derivatives of phenolics extracted from surface waters but had problems with ghost peaks during chromatographic analysis. This phenomenon is usually associated with the derivatization of high molecular weight compounds trapped at the head of the GC column by injections of the TMS reagents. Stallings(37) derivatized and discussed the mass spectral characteristics of chlorophenols, hydroxylated PCBs, and chlorinated phenoxyphenols. Unfortunately, none of the above authors gave efficiency data for the derivatization reaction. Stalling and Murray did report overall recoveries (20-30%), but most losses were attributed to extraction inefficiency rather than incomplete derivatization.

Silylation of phenolic pesticides has also been reported. Wright _et al_. prepared TMS derivatives of 2,4,5-trichlorophenol(38) and 2(2,4,5-trichlorophenoxy)ethanol(39) prior to GC analysis. Electron capture sensitivity for the pesticides listed above was increased 10-fold and 100-fold, respectively, over the unmodified pesticide. During these analyses, detection limits as low as 0.01 ppm were achieved in biological samples. Pentachlorophenol(40) and 2-sec-butyl-4,6-dinitrophenol(41) were detected in milk, blood, urine, tissue, soil, water, and fish after conversion to their TMS derivatives.

Methylation using diazomethane is another common technique in environmental analysis. Pierce(42) _et al_. quantified pentachlorophenol in surface waters by gas chromatographic analysis using solvent extraction and etherification techniques. A recovery of 90% was given for the entire analytical procedure. Low yields have been reported when applying this technique to spent bleach liquors (Appendix A). Lindstrom(43) etherified phenols in a similar matrix using diazomethane. Conversion data were not given, but reproducible yields were achieved. Warner(44) _et al_. reported poor quantitative recoveries when attempting to methylate phenols in sewage sludge extracts with vaporized diazomethane. Very poor yields were achieved with the less acidic compounds. Etherification with methanol using BF_3(45) and acid(46) have also been used for aqueous environmental analyses.

The quantitative methylation of phenolic pesticides is practiced routinely. Howard and Yip(47) evaluated three diazomethane procedures using various nitrophenols. Diazomethane alone was the method of choice. The other two methods (diazomethane in methanol and diazomethane/methanol/HCl) gave substantially lower yields. It was also noted that recovery of dinitrophenol varied with the lot of methanol used.

An aqueous technique using dimethyl sulfate to block phenolic and carboxylic acids has been reported. After etherification, methyl derivatives are extracted into an organic solvent and analyzed. Although both high yields and recoveries are usually achieved, this is a somewhat tedious procedure using toxic reagents and has not been widely practiced.

Sen et al.(48) preferentially etherified the hydroxy group in 3-hydroxy-1-nitrosopyridine using a methyl iodide reagent. Derivatized products were removed from reactants using a water:ethyl acetate extraction procedure. Quantitative recoveries were reported. This reagent should also give good results with amines, amides, and alcoholic compounds under modified reaction conditions. Two other reagents were also tested: diazomethane gave only 30% yield, and dimethyl sulfate in alkaline solution showed 80% recovery.

Chau and coworkers have developed an aqueous acylation technique for phenolic compounds using acetic anhydride in an alkaline bicarbonate solution. The reaction mixture was continuously extracted with hexane to remove products. The original work studied pentachlorophenol derivatization which gave better than 88% recovery.(49) High recoveries have also been reported for 3-trifluoromethylnitrophenol.(50) From subsequent studies, it appears that this derivatization procedure is a general one for phenolic compounds although it does not convert acidic herbicides. This appears to be a particularly attractive technique in that: 1) it is specific to phenols, 2) it takes place in an aqueous medium, 3) products are removed as soon as they are formed, 4) clean reagent blanks have been reported, and 5) both high yields and good recovery have been reported.

The use of several reagents which form ether derivatives has also been reported. Kawahara(51) developed a method for derivatizing hydroxy and carboxylic acid compounds using α-bromo-2,3,4,5,6-pentafluorotoluene (PFT). Conversion of test compounds was nearly quantitative. Chau has used pentafluorobenzyl bromide as a "universal" derivative for acidic compounds.* The same reagent was also recommended by Stalling(52) for the analysis of phenols isolated from biological and aqueous matrices. However, nitrophenols were unreactive towards this reagent. Derivatization in this case was accomplished via extraction followed by diazomethane etherification. These ethers show excellent chromatographic properties, are stable in water and give an excellent ecd response. Derivatization of 2,4-dinitrophenyl and 2,6-dinitro-4-fluoromethylphenyl ethers has also been studied, but low yields were reported.(4)

Carboxylic Acids

Almost without exception, carboxylic acids must be derivatized prior to GC/MS analysis. Although there are now a number of column packings and stationary phases which have been developed for direct GC analysis of unmodified acids, most of these supports exhibit high bleed and are, thus, incompatible with GC/MS.

Diazomethane has been used routinely for the analysis of fatty acids,(53) phenolic acids,(54) phenoxyacetic acids,(55,56) and resin acids in environmental samples. Conversion or recovery data were not given in any of the above studies. Williams(57) has shown that phenolic hydroxy acids do not give uniform yields upon derivatazations due to incomplete methylation of the less reactive hydroxyl group. Acylation of the hydroxyl moiety followed by methylation has been suggested as an alternative approach for the analysis of these materials.

Etherification using BF_3 and acidic methanol solution has also been used for aqueous environmental samples.(58) Storrs(59) found that 2,4-D and its related compounds could not be quantitatively etherified with either HCl/methanol or BF_3/methanol, and hindered benzoic acid derivatives were not methylated at all. Kirkland(60) has shown that methylation of polychlorinated benzoic acids must be carried out with diazomethane since sterically hindered acids cannot be quantitatively derivatized by other reagents.

Chau(61) developed a method for nitrilotriacetic acid (NTA) analysis involving separation from the aqueous matrix by ion exchange, followed by ether formation in acidic isopropanol and GC analysis. Recoveries for the derivatization procedures were greater than 90%. Aue(62) and Larson(63) have both used this method for the quantitative measurement of NTA in surface waters.

Trimethylsilyl derivatives were used by Solzberg and Hume(18) for NTA analysis. Difficulties in the procedure included decomposition of the derivative caused by the presence of trace amounts of water and the inability of the silylating reagent to react in the presence of metal interferences.

Chau and co-workers(64,65) have conducted a series of studies to determine the suitability of several reagents for derivatizing phenoxyalkanoic acids. Reagents tested were pentafluorobenzyl bromide (PFBB) and 2-

chloroethanol catalyzed by either boron trichloride or dicyclohexylcarbodiimide (DCC). In all cases, derivatives were separated from reagents using silica gel chromatography. Pentafluorobenzyl bromide gave the highest recoveries for the 10 herbicidal acids tested. DCC gave quantitative recovery in most cases, while BCl_3 failed to catalyst the reactions of 2,3,6-PDA. Other acids showed an 80 to 100% recovery. All derivatives gave better chromatographic separations than the commonly used methyl analogs. Although PFBB gave rather high reagent blank values, it was the most rapid, easily prepared, and universally applicable of the procedures studied. These advantages, plus high ecd response for the PFBB derivative, have made it the method of choice for herbicidal analysis.

Mierzwa and Witek(66) analyzed several acid pesticides as their 2,2,2-trichloroethane esters. Derivatizaation was achieved using trichloroethanol dissolved in trichloroacetic acid as the reagent. An isooctane:water extraction was used to isolate the pure derivative. Recoveries in excess of 90% were reported.

The most difficult acidic compound to derivatize quantitatively with uniform results are the Krebs cycle acids.(4) The ketonic group produces multiple peaks of keto acids. Methylation and silylation have both been used with only limited success. An alternative approach is to block the keto group with oxime or hydrazone formation followed by the appropriate esterification reaction.

Aldehydes and Ketones

Carbonyl compounds are usually analyzed without derivatization. However, this functional group can sometimes reduce compound stability or cause asymmetric chromatographic peaks. In these cases, the hydrazone or oxime derivatives can be formed. Both of these derivatization reactions are highly specific to aldehyde and ketone moieties.

Hydrazone derivatives are reproducibly prepared by reacting a substituted hydrazine with substrate in the presence of a suitable catalyst. Hoshika chromatographed low molecular weight carbonyl compounds as both their 2,4-dinitrophenyl(67) and pentafluorophenyl hydrazones.(68) In both cases, the reaction was highly specific to aldehydes and ketones and, for most compounds, gave quantitative yields. Only acetaldehyde (80%) and diethyl ketones (85%) showed less than complete conversions.

To form oximes, reagent (hydroxyl or alkoxyl amines) and carbonyl compounds are reacted in pyridine. When possible, the pyridine is removed via evaporation so that the sample may be chromatographed in a more appropriate solvent. Compared with the parent compound, oximes are more stable, and can be further modified chemically according to type of polar group.(4) Oximes give characteristic mass spectra which can be easily interpreted. Unfortunately, oximes react to form both syn- and anti-isomers of disymmetric compounds. The isomer may be only partially separated during chromatography making accurate quantitation difficult.

Amines

Free amines do not chromatograph well due to adsorptive losses and pronounced peak tailing caused by solute-sorbent interactions.

The most commonly used derivatization techniques are acylation, silylation, and the preparation of various condensation products.

Amines are very effectively analyzed as acyl derivatives. The formation of trifluoroacetyl (TFA) derivatives is rapid, reliable, and quantitative. These products exhibit high volatility and good GC properties. A further advantage is the informative mass spectrometric fragmentation patterns characteristic of phenolic and alkyl amine derivatives. Trifluoroacetyl derivatives have been used for the analysis of aliphatic, alicyclic, and aromatic amines, as well as various substituted ureas. Hermann(69) reported excellent recovery and good reproducibility when using this derivative to analyze biogenic amines in aqueous solutions.

Acylation is often used in conjunction with other derivatization techniques for the analysis of polyfunctional compounds. Pentafluorophenyl (PFP), pentafluorobenzyl (PFB), and hexafluorobenzyl (HFB) derivatives have all been used to determine trace levels of amines in biological samples. Bradway and Shafik(70) evaluated 9 different electron capture reagents for the derivatization of aniline and its chlorinated analogs. All derivatization reactions were run at the 50 and 500 ng levels for each aniline. Reaction products were fractionated using silica gel chromatography and then analyzed by GC. Broad, tailing solvent peaks obscured the aniline derivative at the lower concentration for all methods except those using pentafluoropropionic and hexafluorobutyric anhydrides as acylating agents. These reagents were particularly desirable giving quantitative yields and complete recovery under mild reaction conditions. Considering the other reagents tested, bromobenzyl chloride did not react with any of the anilines, pentafluorobenzyl chloride gave multiple reaction products, and the nitrophenyl derivatives gave low yields even under strong reaction conditions.

Amines are not very reactive towards silylating groups. However, quantitative conversion for primary and secondary amines is possible when strongly reactive reagents are used.(15) This technique is useful for analyzing complex mixtures of a variety of polyfunctional compounds.

Pentafluorobenzyl chloroformate(71) is a reagent developed specifically for the analysis of tertiary amines. In the presence of a base catalyst, it couples directly to the amino group (which is dealkylated). The derivative produced is stable in heptane under both acidic and basic conditions,, and shows high ecd sensitivity. Quantitative yields with few side products have been reported.

Hosaika(72) referenced a number of techniques used for derivatization of the amine group. However, he pointed out that all of these methods were developed for high molecular weight amines. In contrast, he used conjugation with 2-dichlorothiophene aldehyde, a sulfur containing Schiff base, for the analysis of low molecular weight primary amines. Yields were quantitative with detection limits to the picogram level.

Amino Acids

A comprehensive review of amino acid analysis using derivatization and gas chromatography has been written by Husek.(73) Because amino acids contain a variety of functional groups of varying reactivities, it is difficult to find a single technique that is useful for the quantitative derivatization of all amino acids. Further, suitable chromatographic columns are limited even for derivatized compounds.

Dual derivatization techniques based on esterification of the carboxyl group, followed by acylation of the amino and other functional groups, have been widely used. Gehrke et al.(74-76) have studied the quantitative aspects of utilizing N-trifluoroacetyl butyl esters for amino acid analysis. They were able to achieve high yields for all tested compounds by varying reaction conditions. The solubility of the amino acid in the alcoholic reagent was the limiting factor for quantitative yields. The ease of reaction depends upon the length of the alcohol chain, the amount of catalyst, temperature, and the quantity of reagents. Acylations were usually carried out using the acid anhydride. In addition to the primary amino group; hydroxyl, secondary amino, guanidine, and indole groups can also be acetylated.

Siezen and Mague(77) used a similar technique to analyze 50 different amino acids as the N-heptafluorobutyryl isobutyl esters. Esterification was effected using an HCl:isobutyl reagent and HFB anhydride was used for N-acylation. Both reactions were run at high temperatures (110°C) for 30 min. Excess reagents were evaporated, residues were redissolved in ethyl acetate, and products were analyzed via GC. Most of the 50 amino acids tested gave single derivatization products in constant yield (relative standard deviation <5%). However, molar responses for cystine, cysteine, arginine, and histidine were less reproducible showing 20-30% relative standard deviation. Further, histidine gave two chromatographic peaks, indicating that both monoacyl and diacyl derivatives were present. Higher temperatures and longer reaction times could have been used to overcome the problems associated with these particular amino acids.

Bada and Lee(78) measured enantiomeric ratios of amino acids from seawater using derivatization-GC techniques. Gehrke *et al.*(79) have developed a method to quantitatively convert amino acids to their TMS derivatives. This is a one-step process and hence should be simpler, more rapid, and less prone to sample loss or contamination than the above described techniques. The active silylating agent, (bis)trimethylsilyl trifluoroacetamide (BSTFA), gave quantitative yields for all amino acids using a variety of derivatization conditions. The procedure adopted produced suitable derivatives fulfilling the authors' specified criteria: (a) no rearrangement or structural alteration of substrate should occur during formation, (b) derivatization reactions should be 95-100% complete, (c) no product should be lost during concentration, (d) derivatives should be stable with respect to time (4-7 days), (e) derivatives should show increased volatility, and (f) derivatives should exhibit little or no reactivity with chromatographic supports.

Specific problems with amino acid derivatization in aqueous environmental samples will depend upon the concentration and fractionation schemes used prior to chemical reaction. If solvent or sorbent extractions accompanied by fractionation based on the acid-base properties of the compound are used, then amino acids of similar properties should be grouped together allowing for uniform derivatization conditions for quantitative yields.

However, if a technique is used that concentrates all amino acids in a single fraction (e.g., ionexchange or freeze-drying), then a more universal derivatization technique is necessary for satisfactory results.

Carbohydrates

Carbohydrates are polyfunctional molecules containing hydroxyl, carbonyl, carboxyl, and amino groups. The abundance of these polar functional groups results in compounds of very low volatility which must be derivatized for gas chromatographic analysis. For these compounds, derivatives specific for certain functional groups can be used, as well as more universal techniques such as silylation or acylation. The presence of polyfunctional groups makes the quantitative preparation of a uniform product difficult and as many as four peaks resulting from anomeric and ring isomerization can result from a single compound.

In complex samples containing a number of sugars, the multiplicity of peaks produced will require extremely high efficiency separation for identifying and quantifying derivatives of very similar structure. Attempts have been made to obtain high resolution on GC columns for the separation of the anomeric derivatives.(80) Zanetta(81) showed that a single analysis on a 2 m packed column was sufficient to separate a mixture of TFA derivatives of the O-methyl glycosides, but the corresponding TFA-monosaccharides could not be resolved. Tesařik(82) found that wall-coated open tubular glass capillary columns gave more complete separations of different TMS sugars. By using two capillary columns with stationary phases of different polarity, he was able to identify 11 sugars in a mixture. Eklund _et_ _al_.(83) produced trifluoroacetyl derivatives of nine different monosaccharides and were able to separate all anomers in this mixture using SE-54 or Carbowax capillary columns. Although some adsorptive losses may occur during chromatographic analysis, calibration curves for glucose, fructose, rhamnose and arabinose were linear to the 0.2 ng level.

An alternative method is to reduce the sugars to the corresponding alcohols followed by derivatization. This yields only a single peak as a result of the destruction of ring structure. However, these alcohols will not distinguish between certain pairs of sugars. Further, Wohl derivatives do not give volatile products for ketoses, thereby limiting their use.(84)

Finally, the preparation of cyclic derivatives such as the boronates has been reported for various carbohydrates,(33) but their utility for environmental analysis has not been explored.

Other methods of analysis for these compounds include: liquid chromatography, ionexchange chromatography and colorimetric techniques. Due to a lack of adequate derivatization methods, one of these procedures may be more promising for carbohydrate analysis in complex environmental samples.

Steroids

The most commonly occurring steroids in contaminated water samples are cholesterol, cholestanol, and coprostanol which are found in municipal sewage waste.(85) These compounds may be analyzed without modification, but volatility, peak shape, and chromatographic separation are usually enhanced by derivatization. Many steroids are commonly analyzed as their TMS derivatives (quantitative yields) with good results. Depending upon the nature of the sample extract; silylation, acylation, or methylation may be used.

CONCLUSIONS

In environmental analysis very little attention has been given to developing good derivatization methods for the quantitation and identification of polar organic compounds. This may, in part, be due to the nature of the analyses. Most extraction methods preferentially concentrate hydrophobic substances, and experimental procedures are often designed to be as simple and rapid as possible, thereby minimizing both the need for and desirability of chemical derivatization techniques. Silylation or esterification using diazomethane are the preferred methods when derivatization is performed. However, due to the complexity of the sample mixture and the nature of possible matrix interferences, quantitative reproducible results are not often achieved. It was the purpose of this review to provide a better understanding of the reactions and processes involved in chemical derivatization, so that these techniques can be used more effectively during environmental trace level analysis. When evaluating each of the procedures in the preceding section, it should be kept in mind that most of these were developed to conform to a specific set of criteria. Many derivatization techniques were originally developed in the biochemical field, with the purpose of analyzing a single compound or closely related group of compounds from a single defined sample matrix. In contrast, we are looking to derivatization as an aid in analyzing any organic compound in a variety of aqueous matrices (drinking, surface, or wastewaters). The important criteria for this objective include: (a) quantitative and reproducible derivative yields for as many compounds as possible over a wide range of concentrations, (b) low sample contamination and artifact formation, (c) insensitivity of the derivatization reaction to sample matrix, and (d) formation of a derivative with characteristic mass spectral fragmentation patterns for compound identification and quantification.

The derivatization techniques employed will depend upon sample concentration and fractionation procedures. However, it does appear that even the most universal derivatization techniques give better results with homogeneous samples in a simple matrix suggesting that extensive fractionation would at least optimize the derivatization step of the entire analytical protocol. Ideally, a fractionation scheme should be employed that would separate compounds according to functional group class, as well as remove inorganic ions and high molecular weight organic interferences. If this were achieved, then optimum derivatization conditions could be applied to each compound class to give quantitative and reproducible yields.

Since the number of polar substituents in a compound increases its water solubility, it may be advantageous to perform derivatization in an aqueous medium. Under these conditions, the acetylation procedure developed by Chau or methylation with dimethyl sulfate would be recommended.

It may be concluded from this review that specific techniques are available for successfully derivatizing most organics which may be found in waters. The limitations for good results will depend upon sample fractionation prior to derivatization. It appears inevitable, at least for polar compounds, that extensive sample manipulation may be necessary for adequate compound identification and quantitation.

REFERENCES

1. Stanley, C. W., J. Agr. Food Chem., 14, 321 (1966).
2. Fales, H. M., T. M. Jaouni, J. F. Babshak, Anal. Chem., 45, 2302 (1973).
3. Schlenk, H., J. L. Gerllerman, Anal. Chem., 32, 1412 (1960).
4. Drozd, J., J. Chromatogr., 113, 303 (1975).
5. Ewing, B. B., E.S.K. Chian, J. C. Cook, C. A. Evans, P. K. Hopke, E. G. Perkins, Monitoring to Detect Previously Unrecognized Pollutants,

Report No. 1, U. S. Environmental Protection Agency, Contract 68-01-3234, October (1975).

6. Horner, J., S.S.Q. Hec, R. G. Sutherland, Anal. Chem., 46, 110 (1974).
7. Darbre, A., Esterification, in Handbook of Derivatives for Chromatography, K. Blau and G. S. King, eds., Heyden Press. London, 39 (1978).
8. Ahuga, S., J. Pharm. Sci., 65, 163 (1976).
9. Kossa, W. C., D. K. McCreary, R. R. Kurtz, Gas-Chrom. Newsletter, 18, 2 (1977).
10. Bailey, J. J., Anal. Chem., 39, 1485 (1967).
11. Bitner, E. D., A. C. Lanser, H. J. Dutton, J. Am. Oils Chem. Soc., 48, 633 (1971).
12. Simmonds, P. G., A. Zlatkis, Anal. Chem., 37, 302 (1965).
13. Woolson, E. A., C. I. Harris, Weeds, 15, 1 (1967).
14. Scoggins, H. S., C. H. Fitzgerald, J. Agr. Food Chem., 17, 156 (1969).
15. Pierce, A. E., Silylation of Organic Compounds: A Technique for Gas-Phase Analysis, Pierce Chemical Co., Rockford, Ill., 1968, p 481.
16. Blau, K., Silylation, in Handbook of Derivatives for Chromatography, K. Blau and G. S. King, eds., Heyden Press, London, 1978, p. 39.
17. Applied Science Laboratories, Gas-Chrom. Newsletter, 16, 1 (1975).
18. Stolzberg, R. J., D. N. Hume, Anal. Chem., 49, 374 (1977).
19. Applied Science Laboratories, Gas-Chrom. Newsletter, 16, 1 (1975).
20. Applied Science Laboratories, Gas-Chrom. Newsletter, 17, 1 (1976).
21. Corey, E. J., A. Venkateswarlu, J. Am. Chem. Soc., 94, 6190 (1972).
22. Blau, K., G. S. King, Acylation, in Handbook of Derivatives for Chromatography, K. Blau and G. S. King, eds., Heydon Press, London, 1978, p. 104.
23. Donike, M., J. Chromatogr., 78, 273 (1973).
24. Rajkowski, K. M., G. D. Broadhead, J. Chromatogr., 69, 373 (1972).
25. Cochrane, W. P., J. Chromatogr. Sci., 13, 246 (1975).
26. McCallum, N. K., R. J. Armstrong, J. Chromatogr., 78, 303 (1973).
27. Khan, S. U., Chemical Derivatization of Herbicides Residues for Gas Liquid Chromatographic Analysis. Chemistry and Biology Research Institute, Ottawa, Ontario, KIA OC6, C.B.R.I. Contribution 849.
28. Khan, S. U., R. Greenhalgh, W. P. Cochrane, J. Agr. Food Chem., 23, 430 (1975).

29. Regis Chemical Co., Regis Lab Notes, 21, 3 (1977).

30. A. Darbre, Cyclization, in Handbook of Chemical Derivatization, K. Blau and G. S. King, eds., Heyden Press, London, 1978, p. 262.

31. Applied Science Laboratories, Gas-Chrom. Newsletter, 17, 1 (1976).

32. Brooks, C. J. W., R. S. Maclean, J. Chromatogr. Sci., 9, 18 (1971).

33. Applied Science Laboratories, Gas-Chrom. Newsletter, 11, 2 (1970).

34. Supelco, Inc., Chromatogr. Lipids, 7, 2 (1973).

35. Cooper, T. M. S., J. R. Wheatstone, Water Research, 7, 1375 (1973).

36. Murray, D. A. J., J. Fish Res. Board Can., 32, 52 (1975).

37. Stalling, D. L., J. W. Hogan. Presented at 25th Annual Conference on Mass Spectrometry and Allied Topics, Washington, DC, May, 1977.

38. Wright, F. C., J. C. Riner, B. N. Gilbert, J. Agr. Food Chem., 17, 1171 (1969).

39. Wright, F. C., J. S. Palmer, J. C. Schlinke, J. Agr. Food Chem., 18, 845 (1970).

40. Stark. A., J. Agr. Food Chem., 17, 871 (1969).

41. McKellar, R. L., J. Agr. Food Chem., 19, 758 (1971).

42. Pierce, R. H., C. R. Brent, H. P. Williams, S. G. Reeves, Bull. Environ. Contam. Toxicol., 18, 251 (1977).

43. Lindström, K., J. Nordin, J. Chromatogr., 128, 13 (1976).

44. Warner, J. S., G. A. Jungclaus, T. M. Engel, R. M. Riggin, C. C. Chuang, Proposed Protocol for E.P.A. Priority Pollutants, U. S. Environmental Protection Agency, Aug., 1978.

45. Manka, J., M. Rebhun, A. Mandelbaum, A. Bortinger, Environ. Sci. Technol., 8, 1017 (1974).

46. Gardiner, J., Analyst, 102, 120 (1977).

47. Howard, S. F., G. Yip, J. Assoc. Offic. Anal. Chem., 54, 970 (1971).

48. Sen, W. P., W. F. Miles, S. Seaman, J. T. Lawrence, J. Chromatogr., 128, 169 (1976).

49. Chau, A. S., J. A. Coburn, J. Assoc. Offic. Anal. Chem., 57, 389 (1974).

50. Coburn, J. A., A. S. Chau, J. Assoc. Offic. Anal. Chem., 59, 862 (1976).

51. Kawahara, F. K., Anal. Chem., 40, 2073 (1968).

52. Stalling, D. L., L. M. Smith, J. O. Petty, Symposium on Measurement of Organic Pollutants in Water and Wastewater, ASTM, Denver, Colorado, June, 1978.

53. Budde, W., Solubility Separation by pH Adjustment: A Procedure for the Extraction of Industrial Organic Chemicals in Effluents and Streams, U. S. Environmental Protection Agency.

54. Rockwell, A., Larson, R. A. in Water Chlorination, R. L. Jolley, H. Gorchev and D. H. Hamilton, eds., Ann Arbor Science, Inc., Ann Arbor, MI, 1978, p. 67.

55. Cook, G. H., J. C. Moore, J. Agr. Food Chem., 24, 631 (1976).

56. Hattula, M. S., S. Raisanen, Bull. Environ. Contam. Toxic., 16, 355 (1976).

57. Williams, C. M., Anal. Biochem., 11, 224 (1965).

58. Renberg, L., Anal. Chem., 46, 459 (1974).

59. Storrs, E. E., H. P. Burchfield, Anal. Chem., 34, 423 (1962).

60. Kirkland, J. J., Anal. Chem., 33, 1520 (1961).

61. Chau, Y. K., M. E. Fox, J. Chromatogr. Sci., 9 (1971).

62. Aue, W. A., C. R. Hastins, K. O. Gerhardt, J. O. Pierce, H. H. Hill, R. F. Moseman. J. Chromatogr., 72, 254 (1972).

63. Larson, R. A., J. C. Weston, S. M. Howell, J. Chromatogr., 111, 43 (1975).

64. Chau, A. S., K. Terry, J. Assoc. Offic. Anal. Chem., 58, 1246 (1975).

65. Agemain, H., A. S. Chau, J. Assoc. Offic. Anal. Chem., 60, 1070 (1977).

66. Mierzwa, S., S. Witek, J. Chromatogr., 136, 105 (1977).

67. Hoshika, Y., J. Chromatogr., 152, 224 (1978).

68. Hoshiki, Y., J. Chromatogr., 120, 279 (1976).

69. Hermann, V., T. Juttner, J. Chromatogr., 78, 3675 (1977).

70. Bradway, D. E., T. Shafik, J. Chromatogr. Sci., 15, 322 (1977).

71. Hartvig, P., Vessman, Anal. Letters, 7, 223 (1974).

72. Hoshika, Y., J. Chromatogr., 136, 253 (1977).

73. Husek, P., K. Macek, J. Chromatogr., 113, 139 (1975).

74. Gehrke, C. W., F. Sharokhi, Anal. Biochem., 15, 97 (1966).

75. Gehrke, C. W., D. L. Stalling, Separ. Sci., 3, 101 (1967).

76. Gehrke, C. W., R. W. Zumwalt, L. L. Wall, J. Chromatogr., 37, 398 (1968).

77. Siezen, R. J., T. H. Hague, J. Chromatogr., 130, 151 (1977).

78. Lee, C., J. Bada, Limnol. and Ocean, 22, 502 (1977).

79. Gehrke, C. W., H. Nakamoto, R. Zumwalt, J. Chromatogr., 45, 24 (1969).

80. Lochmuller, C. H., R. W. Souter, J. Chromatogr., 113, 283 (1975).

81. Zanetta, J. P., Breckenridge, G. Vincendon, J. Chromatogr., 69, 291 (1972).

82. Tesařik, K., J. Chromatogr., 69, 295 (1972).

83. Eklund, G., B. Josefsson, C. Roos, J. Chromatogr., 142, 575 (1977).

84. Szafranek, J., C. D. Pfaffenberger, E. C. Horning, Anal. Lett., 6, 479 (1973).

85. Sheldon, L., R. Hites, Environ. Sci. Technol., 12, 1188 (1978).

SECTION 7

GAS CHROMATOGRAPHY

Successful identification and quantitation of analytes in complex environmental samples require good chromatographic separations. Both packed and capillary chromatography columns have been used for this purpose.

Packed columns usually consist of a solid support coated with a liquid phase packed into a short (~180 cm) 2 mm ID column. They are relatively easy to work with, inexpensive to make, and available in many liquid phase/solid support combinations which can be tailored toward a given analysis. Because of these advantages and their high loading capacity, packed columns are routinely used for environmental analysis. However, they do possess several inherent disadvantages. Columns with a high loading of liquid phase tend to bleed and, therefore, a number of good gas chromatographic liquid phases (DEGS, FFAP, etc.) are incompatible with GC/MS instrumentation. Also, and most importantly, packed columns are low resolution columns which often give incomplete separations of complex mixtures.

Capillary columns provide an alternative to packed column chromatography. Wall coated open tubular columns (WCOT) are narrow bore (0.2 to 1.0 mm ID) glass columns varying in length from ten to one hundred meters. The most significant difference between capillary columns and packed columns is that the liquid phase is coated directly onto the surface of the capillary column to provide increased chromatographic resolution. Under these conditions both packing and multiflow factors are minimized to provide more efficient columns (lower HETP). Furthermore, capillary columns can be prepared at significantly greater lengths than packed columns since pressure drops associated with packed columns severely limit carrier gas flow.

Although capillary columns have always provided high separation efficiencies, problems with adsorption and degradation of sample components, limited availability of chromatographic phases, rapid column deterioration, and problems with column and sample handling have limited their use. However, recent developments in column technology, coating procedures, and injection techniques have resulted in greater acceptance for routine analytical work. Advances in capillary column technology are well-documented in numerous review papers(2-5) and monographs.(1,6) These papers discuss capillary column technology and glass surface chemistry,(4) preparation techniques,(2,4) capillary column performance characteristics,(1,4) and selected environmental applications.(3) This review will briefly discuss column properties, chromatographic instrumentation, and environmental applications.

COLUMN PROPERTIES

Two properties of glass surfaces are incompatible with the preparation of capillary columns. First, smooth surfaces may prevent the formation of a homogenous thin film of the liquid phase. Second, active sites within the glass structure may cause adsorption and catalytic degradation of organic compounds. All of the existing methods for wall modifications are directed toward changing these properties. Reviews by Grob,(7) Jennings,(1) and Verzele(8) provide a good overview of the subject.

Wettability--

Chromatographic theory demonstrates that maximum separation efficiency is achieved with a homogenous thin film of liquid phase coated uniformly on the surface of the column walls.(9,10) However, since the cohesive forces of the liquid are usually greater than the adhesive or wetting forces between the liquid and glass surface, the liquid tends to draw up in discrete globules or beads. Therefore, some method of film stabilatization is required to maintain liquid phase uniformity necessary for optimum column efficiency.

The simplest method of film stabilization is to lower the surface tension of the liquid phase by adding a surfactant. Wetting agents most commonly used include quaternary ammonium compounds,(11) phosphonium compounds,(12) nonionic detergents,(13) and small additions of highly polar liquid phases.(14)

The alternative to modifying the liquid phase is to alter the surface of the solid support. Physical modifications usually alter the roughness of the glass surface whereas chemical modifications change the molecular/ionic structure of the surface.

On a roughened surface, liquid phase will accumulate in the cavities of the support as a result of capillary action. This produces a quasi-film consisting of adjacent pools or droplets. Since maximum separation efficiency is possible only with homogeneous thin films, a measurable loss in column efficiency is observed. Depending upon treatment, the shape of the roughened surface may vary significantly. The most successful methods of surface roughening include hydrochloric acid etching,(15-20) whisker formation,(20-25) deposition of sodium chloride,(26-28) formation of a barium carbonate layer,(29-31) and hydrochloric acid leaching.(32-36) At present, the relationship between surface geometry (shape, depth, and width of roughness) and the quality and stability of coated films is unknown.(7)

Chemical modifications alter the support surface thereby increasing intermolecular attractions between surface functional groups and the stationary phase. Cold silylation has been attempted by several researchers as a method for chemically modifying glass surfaces. Traditional silylating reagents(21,37,38) produce very nonpolar surfaces with poor wetting properties. Novotny _et al_.(39,40,41) tried to adapt the silylating reagent by incorporating chloroalkyl, cyanoalkyl, and other groups into the reagent to improve surface wettability. Welch,(42) and Grob(33,34) have both reported methods for high temperature silylation of wall surfaces. Although, only nonpolar TMS reagents have been used to date, it is anticipated that modifying the reagent with polar groups should serve to improve surface wettability.

Activity

Surface activity may be considered the sum of influences which the molecular/ionic structure of the support surface exerts on both the coating and the sample. Activity is due to individual functional groups or ions rather than the surface as a whole. The most obvious effect of surface activity is adsorption of sample components; however, catalytic degradation of sample components may also occur. A third effect of surface activity is catalytic decomposition of the stationary phase to reduce the thermal stability of the column. High temperature treatment with Carbowax 20M,(43-46) and high temperature persilylation(47) have been used efficiently to produce deactivated columns with high thermal stability.

Gas phase Carbowax deactivation was first developed by Cronin,(43) but many variations now exist. During the procedure, pyrolysis of Carbowax produces oxirane which then blocks silyanol (-Si-O-H) functional groups. Carbowax deactivation has two important limitations. First, it does not really deactivate the surface, but rather reduces or controls activity. Second, since it merely covers active sites, the catalytic activity of these sites acts on the Carbowax coating to reduce its thermal stability.

During high temperature persilylation, the column is first acid-leached at elevated temperature. Grob(28) has used 20% HCl at 240°C overnight to effect leaching of soft glass tubing. During this process, the silicon, oxygen, and siloxane bonds are replaced by silanol functional groups. The glass matrix is opened and metal ions are eliminated to produce a hydrated silica surface. Since metal oxides can serve as catalytic sites for organic decomposition, leaching eliminates many of the active sites on the surface of glass capillary columns. During preparation of silanized columns, leaching is followed by dehydration. This eliminates excess moisture which would otherwise react with the reagent to give a high ammonia concentration. Silanization is then performed at an elevated temperature. Grob(29) reports producing columns with low surface activity and high temperature stability using this technique.

The recently introduced fused silica columns are highly inert, particularly in comparison to glass materials.(47,48) Fused silica contains very low levels of metal oxides; thereby substantially reducing the number of active sites within a column. As with other glass columns, Carbowax 20M, persilylation, and dehydroxylation(49) have been used to decrease residual surface activity. The interrelationship of surface energies, deactivated surfaces, and wettability by stationary phases in fused silica columns has been investigated.(50,51) The low surface energy of fused silica prohibits coating with highly polar stationary phases. Columns coated with phases more polar than Carbowax 20 M are not reported. The low surface energy of the substrate does not permit easy fabrication of columns with thick films, although columns with 0.5 μ film thicknesses are now available commercially.

Grob has discussed the relationship between polarity of the liquid phase and the surface requirements for producing stable films.(7) This information is summarized as follows:

(1) Nonpolar coatings are stable on any surface, including active-smooth, active-rough, and inactive-rough surfaces.

(2) Semipolar coatings require roughened surfaces. They may be stable on inactive-rough and on active-rough; but not on active-smooth surfaces.

(3) Polar coatings require active-rough surface for film stabilization.

Column Coating

Coating procedures are designed to deposit a uniform film throughout the column, usually from 0.1 to 1.5 μ thick. General procedures for both static and dynamic coating procedures have been reviewed in detail.(1)

Chemically bonded phase or high temperature cross-linked stationary phase columns are becoming increasingly popular, especially for on-column and splitless injection where associated large solvent volumes could rapidly deterioriate the performance of conventionally coated columns. Blomberg reported(52-54) the *in situ* synthesis of bonded films by cross-linking methyl and phenyl siloxanes. The stationary phases were insoluble in commonly used solvents and showed good thermal stability. Grob(55,56) and Sandra(57) used organic peroxides to initiate cross-linking and to immobilize silicon on the surface of the column. Chemically bonded fused silica columns are now available from several manufacturers.

CHROMATOGRAPHIC TECHNIQUES

In packed column chromatography, the sample is vaporized in the GC injection port and quickly swept onto the head of the column with the carrier gas. Because the flow rate of carrier gas is high (20-30 mL/min) and the chromatographic peaks are generally broad, no significant deterioration in peak shape associated with the injection process is noted. However, during capillary chromatography, the flow rate of carrier gas is significantly reduced (≥2 mL/min). At these flow rates, the band of material deposited onto the head of the column would be three to five minutes wide and each sample component that begins the chromatographic process immediately on injection will produce a peak of at least this width. Special injection techniques for capillary chromatography have been developed to circumvent this problem and include stream splitting, splitless injection and on-column injection.

Splitting the flow stream gives a high flow through the vaporization chamber to rapidly flush it clean while maintaining restricted flow through the column. In addition, since WCOT columns have low sample capacity, split injections provide a method for introducing small amounts of sample material onto the column while, at the same time, allowing injection of sufficient sample to minimize injection errors. A number of splitter designs have been described(58,59) and the criteria for evaluating splitter linearity are also available.(60,61)

Theoretically, the split ratio for all components of a sample should be equal to the ratio of the flow through the column to the flow through the splitter to the exhaust. In order to achieve this, samples should be vaporized, thoroughly mixed, and then undergo expansion just prior to splitting. Optimally, all components of the splitter should be glass to avoid sample decomposition, and should be removeable for periodic cleaning and deactivation. In practice, the actual split ratio, as well as the linearity of the split over the entire sample range will vary with injector design, injection techniques, and sample type.(62)

Adequate sample vaporization is essential to prevent discrimination against high boiling compounds. In order to assure vaporization prior to splitting most injectors are modified by introducing glass wool, glass beads or GC packing material into the injector. Schomburg *et al*. reviewed and investigated several of these modifications.(63) Several general trends were concluded from their study. First, although GC packing material in the injector adequately homogenizes the sample, it provides greatest potential for sample decomposition and adsorptive losses. Second, although all-glass constructions (*i.e*., those with no packing) are the most inert they afford poorer sample vaporization and hence greater volatility discrimination. Finally, the use of deactivated glass wool packings is the preferred method showing the best accuracy and precision during split without providing a very large surface area for sample adsorption or decomposition. The length, tightness, and position of the glass wool plug were also varied in relation to the position of the syringe needle at injection and priority to the splitting region with the best results achieved with a fully packed injector.

Other factors which influence vaporization of the sample components are the temperature of the injection port and injection technique. Obviously, the injector port must be hot enough to vaporize the samples components. At high split ratios, heating the carrier gas prior to sweeping it through the vaporization chamber is often recommended. Grob, *et al*.,(63) have demonstrated that for stream splitting, a hot needle injection provides greatest linearity between the amount of a given component injected and the amount detected.

The stream splitting technique has improved over the last several years to allow accurate quantitative determinations and adequate split injectors are now commercially available. However, both dilute samples and samples containing a high fraction of less volatile components can best be handled using alternate techniques, namely: splitless or on-column injection.

Splitless injection is a variant of stream splitting which allows introduction of the entire injected sample onto the capillary column without causing loss of separation efficiency or solvent peak spreading. Splitless injection involves injecting several microliters of sample into the vaporization chamber while the capillary column is relatively cool. During injection and subsequent transfer of the sample onto the column, the splitting valve remains closed. After the bulk of the sample has been transferred onto the column (one to two minutes), the splitting valve is opened to purge the vaporizer chamber, the septum, and the fittings. If the boiling point of the injected solvent is at least 20°C higher than the column temperature, the solvent will condense in the first section of the column and aid in peak resolution.(65,66,67)

The principle behind this solvent effect was first described by Harris.(68) Briefly, the vaporized material is transferred onto the column as a mixture. During initial migration, the solvent shifts away from the sample components leaving them on the back slope of the large peak. As the chromatographic process continues, the moving vapor plug of the sample components meets a liquid phase mixed with retained solvent. The front of the sample plug moving forward through the column continues to encounter an ever-increasing concentration of solvent and as a consequence is more strongly retained than in the rear of the plug. Hence, band narrowing should occur under properly executed splitless injection.

The special nature of the solvent effect is due to the overwhelming amount of solvent present compared with the amounts of the sample components. In the first stage of analysis, this amount becomes comparable with the amount of stationary phase in the inlet port of the column.

The salient features of the splitless injection can be summarized as follows.(67)

(1) Splitless injection relies upon a solvent effect rather than cold trapping, such that both isothermal and temperature programmed GC can be used.

(2) A critical volume of sorbent is necessary to achieve adequate focussing.

(3) Under proper conditions, the solvent peak will obscure only the peaks of those substance which would be eliminated together with the solvent.

(4) On capillary columns with a stable coating, large amounts of solvent can be injected daily without adverse effects on the column.

(5) The most universal solvents for injection without splitting at room temperature are carbon disulfide, and methylene chloride.

(6) There is a critical and relatively narrow temperature range for the capillary column for each solvent.

(7) The detailed mechanism of plug concentration is different for polar and nonpolar solvents.

(8) The concentration effect sharpens only those peaks which elute later than the solvent; earlier eluting peaks have broad profiles.

(9) Finally, large amounts of solvent condensed in the column inlet change the polarity of the liquid phase such that retention times of sample components may be changed.

Although splitless injection appears to be an improved technique over stream-splitting, especially for dilute samples, it still suffers several drawbacks. The transfer of high-boiling sample components may not be complete when the split valve is opened, thereby distorting sample linearity. Furthermore, long residence times in a heated vaporization chamber may cuase decomposition of heat-labile sample components. Alternatively, on-column injection introduces the sample directly into the capillary column without previous vaporization outside the column.(64) This mode of injection eliminates problems of homogenization in split sampling and of sample vapor transfer in splitless sampling to give a more representative chromatogram. By eliminating the need for sample vaporization, problems with thermal decomposition, sample adsorption, and sample reproducibility are also minimized. Finally, on-column injection eliminates the need for a septum on the injection port. This should minimize the temporary adsorption and, subsequent, release of vaporized sample components which results in impaired resolution. Contamination from septum bleed should also be reduced.

Several techniques for sample introduction and/or volume adjustment have been described for on-column sampling. Two different techniques were proposed by Schomburg for either small (<0.1 μL) or large (0.5-20 μL) sample volumes.(64) As an alternative, Grob(71) proposed the use of a special injector for on-column introduction through a microsyringe. Temporary additional cooling of the syringe has been used to prevent selective evaporation of the sample components.(72) Schomburg, on the other hand, used a sampling crucible with a full pressure-lock system. This recently introduced technique greatly reduces discrimination of high boiling components, improves chromatographic precision, and eliminates degradation of thermally labile compounds in vaporizer injectors.

COLUMN EVALUATIONS

Ideally, capillary columns should possess a high separation efficiency, good tailing behavior and high temperature stability.(73,74) In order to demonstrate these properties, several evaluation procedures have been proposed. For example, in testing columns, the symmetry of peaks of selected test compounds which are contained in so-called "polarity mixtures" provide information on film thermal stability. The difficulty in properly evaluating capillary columns lies in the choice of test compounds, chromatographic conditions and meaningful measurements. Grob et al.,(75) listed the following criteria for an adequate column test:

(1) the test should consist of a single chromatographic run;
(2) the test mixture should contain all of the components necessary to give all of the basic information required;
(3) the same test should be applicable to all liquid phases;
(4) some quantitative aspects should be included; and
(5) conditions should be standardized so as to make test results comparable.

Different polarity mixtures have been suggested by Grob et al.,(75,76) Schomburg et al.,(77) Alexander et al.,(78) Hartigan and Ettre,(79) Sandra and Verzele,(80) Welsch et al.,(42) Cram et al.,(81) De Nijs et al.(82) and Dandeneau and co-workers.(47) These mixtures contain components with a variety of functional groups. Saturated hydrocarbons, alcohols, aromatic compounds, aldehydes, phenols and amines have been widely used.

Since most chromatographic separations on glass capillary columns are performed at elevated temperatures or employ temperature programming, the temperature stability of a coated glass capillary column is of utmost importance. For a column to perform satisfactorily at higher temperatures the coated stationary phase must remain stable. That is, its decomposition must be minimal and it must remain as a thin, uniform surface film, and not break up into droplets. In addition, the surface beneath the stationary phase, i.e., the deactivation layer must remain stable. In fact, the temperature stability of the deactivation layer is as important as the stability of the stationary phase itself. As suggested by Schomburg and co-workers,(83) the following properties should not deteriorate or change substantially during extended high temperature operation:

(1) The capacity ratio (k) should not decrease significantly (indicating that the stationary phase is not decomposing to any great extent).

(2) The separation efficiency in terms of theoretical plates per meter should remain essentially constant (indicating that the quality and integrity of the stationary phase film is not being disrupted).

(3) The background signal arising from bleed products should remain constant and not exceed a defined limit (also indicating that the stationary phase and/or deactivating pre-coating layers are not decomposing significantly).

(4) The polarity in terms of retention indices of standard compounds should remain constant (indicating that the chemical nature of the stationary phase and/or the deactivation is not changing).

(5) The extent of surface deactivation toward strongly polar solutes when using a polar stationary phases should remain stable. That is, the tailing behavior and adsorption of polar solutes at trace concentration levels should not become more pronounced after high temperature operation of the column.

ENVIRONMENTAL APPLICATIONS

The use of capillary columns and, in particular, fused silica capillary columns is becoming increasingly popular for environmental analysis. Fused silica capillary columns offer several significant capabilities not provided by packed columns and borosilicate capillary columns. First, they are high resolution columns which should allow the analysis of more complex sample mixtures or allow very rapid analysis of less complex mixtures.(84,85) Second, they are chemically inert. chromatographic separation of underivatized phenols has been reported for less than 1 ng of material per injections by several workers.(86,87) Third, the use of chemically bonded phases now provides durable columns. Fourth, the flexible fused silica material allows easy handling of columns. Finally, direct coupling of fused silica capillary columns to the injector and the ion source of the mass spectrometer avoids unnecessary connection, "dead volumes," and reactive surfaces which significantly impair overall chromatographic performance.(8)

Although the Priority Pollutant Protocols(89,90) currently specify using packed columns for the analysis of volatile and semivolatile analytes. EPA is currently evaluating fused silica capillary columns for this purpose. During these evaluations, mass spectral response factor precision was reported for the extractable priority pollutant phenols including the very acidic dinitrophenols.(88) In an effort to shorten GC/MS analysis time, the acid, base/neutral, and pesticide priority pollutant fractions were combined and analyzed simultaneously.(91,92) Chromatograms showed good analyte separation with excellent response factor precision. Excellent precision was also reported for relative retention time which should improve the efficiency and reliability of quantitative GC/MS analysis. During one study using a fused silica capillary column, the recognition rate, i.e., the number of spectra automatically identified relative to the number of spectra detected was increased by approximately a factor of two over packed column data acquired previously.(93,95) Several laboratories have reported success using this method for priority pollutant analysis.(91-95)

Work is currently being performed to develop quality assurance protocols for the use of fused silica capillary columns during priority pollutant analysis.(96) The protocols will outline column specifications, installation and operation details, and criteria for system calibration and retention time reproducibility. Fused silica capillary columns have been used for the analysis of a wide variety of organic compounds other than priority pollutants, including PCBs,(97,98) phenols,(86,87,99) derivatized acids,(99,100) amines,(99,100) and polar and nonpolar neutral(99-103) compounds.

APPENDIX B, as a general guideline, lists the various chromatographic liquid phase coatings that have been used for analysis of organics in water, according to chemical class. In addition, the type of column and the type of water in which the chemical was found are listed.

REFERENCES

1. Jennings, W. G., Gas Chromatography with Glass Capillary Columns, 2nd Ed., Academic Press, New York, 1980.
2. Alexander, G., Chromatographia, 14, 55 (1981).
3. Cram, S. P., F. J. Yang, Adv. Chem. Ser., 185, 105 (1980).
4. Lee, M. L., B. W. Wright, J. Chromatogr., 184, 235 (1980).
5. Schomburg, G., Anal. Chem. Symp. Ser., 3, 327 (1980).
6. Jennings, W. G., Comparisons of Fused Silica and Other Glass Columns in Gas Chromatography, Huethig, Heidelberg, Fed. Rep. Ger., (1981).
7. Grob, K., G. Grob, J. Chromatogr., 125, 471 (1976).
8. Verzele, M., J. High Resol. Chromatogr. and Chromatogr. Comm., 2, 647 (1979).
9. Giddings, C., Anal. Chem., 34, 458 (1962).
10. Giddings, C., Anal. Chem., 35, 439 (1963).
11. Metcalfe, L. D., R. J. Martin, Anal. Chem., 39, 1204 (1967).
12. Malec, E. J., J. Chromatogr. Sci., 9, 318 (1971).
13. Mon, T. R., R. R. Forrey, R. Teranishi, J. Gas Chromatogr., 5, 497 (1967).
14. Jennings, W. G., Chem. Mikrobiol., Technol. Libersm., 1, 9 (1971).
15. Alexander, G., G. Garzo, G. Palyi, J. Chromatogr., 91, 55 (1974).
16. Badings, H. T., J. J. G. van der Pol, J. G. Wassink, Chromatographia, 8, 440 (1975).
17. Franken, J. J., G. U. F. Rutten, J. A. Rijks, J. Chromatogr., 126, 117 (1976).
18. Krupcik, J., M. Kristin, M. Valachoveccva, S. Janiga, J. Chromatogr., 126, 147 (1976).
19. Badings, H. T., J. J. G. van der Pol, D. G. Schmidt, Chromatographia, 10, 404 (1977).
20. Tesarik, K., M. Novotny, in H. G. Struppe, ed., Gas Chromatographie 1968, Akademie Verlag. Berlin, 575 (1968).
21. Novotny, M., K. Tesarik, Chromatographic, 1, 332 (1968).

22. Schieke, J. D., N. R. Comins, V. Pertorius, Chromatographia, 8, 345 (1975).

23. Schieke, J. D., N. R. Comins, V. Pretorius, J. Chromatogr., 112, 97 (1975).

24. Schieke, J. D., N. R. Comins, V. Pretorius, J. Chromatogr, 115, 373 (1975).

25. Sandra, P., M. Verzele, Chromatographia, 10, 419 (1977).

26. Watanabe, C., H. Tomita, J. Chromatogr. Sci., 13, 123 (1975).

27. Watanabe, C., H. Tomita, J. Chromatogr., 121, 1 (1976).

28. Sandra, P., M. Verstappe, M. Verzele, Chromatographia, 11, 223 (1978).

29. Grob, K., G. Grob, J. Chromatogr., 125 471 (1976).

30. Grob, K., G. Grob, K. Grob, Jr., Chromatographia, 10, 181 (1977).

31. Grob, K., J. R. Guenter, A. Portmann, J. Chromatogr., 147, 111 (1978).

32. Onuska, F., M. Comba, Second International Symposium on Glass Capillary Chromatography - Hindelang, R. E. Kaiser, ed., 283 (1977).

33. Grob, K., G. Grob, K. Grob, Jr., J. High Resolut. Chromatogr. Chromatogr. Commun., 2, 31 (1979).

34. Grob, K., G. Grob, K. Grob, Jr., J. High Resolut. Chromatogr. Chromatogr. Commun., 2, 677 (1979).

35. Grob, K., J. High Resolut. Chromatogr. Chromatogr. Commun., 3, 197 (1980).

36. Grob, K., J. High Resolut. Chromatogr. Chromatogr. Commun., 3, 493 (1980).

37. Novotny, M., L. Blomberg, K. Bartle, J. Chromatogr. Sci., 8, 390 (1970).

38. Rutten, G., J. A. Luyten, J. Chromatogr., 68, 55 (1972).

39. Novotny, M., K. D. Bartle, Chromatographia, 3, 272 (1970).

40. Novotny, M., K. Grohmann, J. Chromatogr, 84, 167 (1973).

41. Bartle, K. D., M. Novotny, J. Chromatogr, 94, 35 (1974).

42. Welsch, T., W. Englewald, Ch. Klaucke, Chromatographia, 10, 22 (1977).

43. Cronin, D. A., J. Chromatogr., 97, 263 (1974).

44. Blomberg, L., T. Wannman, J. Chromatogr., 148, 379 (1978).

45. Franken, J., R. C. M. de Nijes, F. L. Schulting, J. Chromatogr., 144, 253 (1977).

46. de Nijes, R. C. M., J. J. Franken, R. Dooper, J. A. Rykes, H. J. de Ruive, F. L. Schutling, J. Chromatogr., 167, 231 (1978).

47. Dandeneau, R., E. H. Zerenner, J. High Resolut. Chromatogr. Chromatogr. Commun., 2, 351 (1979).

48. Godefroot, M., M. Van Rodenbosch, M. Verstappe, P. Sandra, M. Verzele, J. High Resolut. Chromatogr. Chromatogr. Commun., 3, 337 (1980).

49. Pretorius, V., D. H. Desty, J. High Resolut. Chromatogr. Chromatogr. Commun., 4, 38 (1981).

50. Lipsky, S. R., W. McMurray, M. Hernandez, J. Purcell, K. Bellele, J. Chromatogr. Sci., 18, 1 (1980).

51. Lipsky, S. R., W. McMurray, op. cit., R. E. Kaiser, ed., 505 (1981).

52. Blomberg, L., K. Markides, T. Waenman, J. High Resolut. Chromatogr. Chromatogr. Commun., 3, 527 (1980).

53. Blomberg, L., T. Waennman, J. Chromatogrt., 186, 159 (1979).

54. Blomberg, L., K. Markides, T. Waennman, J. Chromatogr., 203, 217 (1981).

55. Grob, K., G. Grob, K. Grob, Jr., J. Chromatogr., 211 243 (1981).

56. Grob, K., G. Grob, K. Grob, Jr., J. Chromatogr. Commun., 3, 493 (1980).

57. Sandar, P., G. Redant, E. Schacht, M. Verzele, J. High Resolut. Chromatogr. Chromatogr. Commun., 4, 411 (1981).

58. Ettre, L. S., Open Tubular Columns in Gas Chromatography, Plenum, New York (1965).

59. Halasz, I., W. Schneider, Anal. Chem., 33, 979 (1961).

60. Jennings, W. G., J. Chromatogr. Sci., 13, 186 (1975).

61. Ettre, L. S., W. Averill, Anal. Chem., 33, 680 (1961).

62. Condon, R. D., L. S. Ettre, in Instrumentation in Gas Chromatography, J. Krugers, ed., Centrex Publ., Eindhoven, Netherlands, 87 (1968).

63. Grob, K., Jr., H. P. Neukom, J. High Resolut. Chromatogr. Chromatogr. Commun., 2, 563 (1979).

64. Schomburg, G., H. Behlaur, R. Dielmann, F. Weeke, H. Husmann, J. Chromatogr., 142, 87 (1977).

65. Grob, K., G. Grob, Chromatographia, 5, 3 (1972).

66. Grob, K., K. Grob, Jr., J. Chromatogr., 94, 53 (1974).

67. Grob, K., K. Grob, Jr., J. High Resolut. Chromatogr. Chromatogr. Commun., 1, 57 (1978).

68. Harris, W. E., J. Chromatogr. Sci. 11, 184 (1973).

69. Schomburg, G. H. Husmann, R. Rittmann, J. Chromatogr., 204, 85 (1981).

70. K. Grob, G. Grob, J. High Resolut. Chromatogr. Chromatogr. Commun., 1, 263 (1978).

71. Grob, K., K. Grob, Jr., J. Chromatogr., 151, 311 (1978).

72. Galli, M., S. Trestiani, K. Grob., J. High Resolut. Chromatogr. Chromatogr. Commun., 2, 366 (1979).

73. Schomburg, G., H. Hussmann, Chromatographia, 8, 517 (1975).

74. Schomburg, G., H. Hussman, F. Weeke, Chromatographia, 10, 580 (1977).

75. Grob, K., Jr., G. Grob, K. Grob, J. Chromatogr., 156, 1 (1978).

76. Grob, K. G. Grob, Chromaotgraphia, 4, 422 (1971).

77. Schomburg, G. H. Hussman, F. Weeke, J. Chromatogr., 99, 63 (1974).

78. Alexander, G., G. Garzo, G. Palyi, J. Chromatogr., 91, 25 (1974).

79. Hartigan, M., L. S. Ettre, J. Chromatogr., 119, 187 (1976).

80. Verzele, M., P. Sandra, J. Chromatogr., 158, 111 (1978).

81. Cram, S., F. Yang, A. Brown, Chromatographia, 10, 397 (1977).

82. de Nijes, R. C. M., G. Rutten, J. Franken, R. Dooper, J. Rijks, J. High Resolut. Chromatogr. Chromatogr. Commun., 2, 447 (1979).

83. Schomburg, G., R. Dielmann, H. Borwitzky, J. Chromatogr., 167, 337 (1978).

84. Rooney, T. A., L. Altmijyer, L. Freeman, E. C. Zerenner, Am. Lab., 11, 81 (1979).

85. Wright, B., M. Lee, J. High Resolut. Chromatogr. Chromatogr. Commun., 3, 352 (1980).

86. Giger, W., C. Schaffner, in Advances in the Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Volume 1, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 141 (1981).

87. Freeman, R. R., ibid., 155 (1981).

88. Sauter, A. D., L. Belowski, T. Smith, V. Strickler, R. Beimer, B. N. Colby, J. E. Wilkinson, J. High Resolut. Chromatogr. Chromatorg. Commun., 4, 366 (1981).

89. "Purgeables - Method 624," Federal Register, 44, No. 233, 69532, Monday, December 3, 1979.

90. "Acids - Base/Neutrals - Method 624," Federal Register, 44, No. 233, 69536, Monday, December 3, 1979.

91. Sauter, A., L. Belowski, M. Heatt, M. E. Meier, Proceedings of the 28th Annual Meeting at the American Society of Mass Spectrometry, New York, NY, 168 (1980).

92. Sauter, A. D., L. Belowski, B. Colby, J. Wilkinson, T. Smith, Pittsburg Conference, Atlantic City, NJ, March 1981.

93. Shackelford, W. M., Proceedings of the Seminar for Analytical Methods for Priority Pollutants, U. S. E. P. A., Effluent Guidelines Division, Hershey, PA, 1981, in press.

94. Trussel, A. R., F. Y. Lieu, J. C. Moncur, op. cit., L. Keith, ed., Volume 1, 171 (1981).

95. Colby, B. N., presented at National Meeting, American Chemical Society, Las Vegas, NV, March 1982.

96. Lopez-Avela, V., presented at National Meeting, American Chemical Society, Las Vegas, NV, March 1982.

97. Mullen, M. D., J. C. Filkins, op. cit., L. Keith, ed., Volume 1, 187 (1981).

98. Pellizzari, E., K. Tomer, A. Moseley, ibid., 197 (1981).

99. Sheldon, L., R. Zweidinger, M. Jones, M. Warner, P. Hyldburg, E. Pellizzari, presented at National Meeting, American Chemical Society, Las Vegas, NV March 1982.

100. Garrison, A. W., E. D. Pellizzari, presented at National Meeting American Chemical Society, Las Vegas, NV March 1982.

101. Hunt, G. T., M. Hayte, presented at National Meeting, American Chemical Society, Las Vegas, NV, March 1982.

102. Beimer, R. G., M. K. O'Rell, A. D. Sauter, presented at National Meeting, American Chemical Society, Las Vegas, NV, March 1982.

103. Trussel, A. R., T. Lieu, J. G. Moncur, presented at Second Chemical Congress of the North American Continent, San Francisco, August 1980.

SECTION 8

GAS CHROMATOGRAPHY/MASS SPECTROMETRY/COMPUTER TECHNIQUES

INTRODUCTION

Two of the most crucial aspects of environmental analysis are the determination of the identity of substances that are contained in an environmental sample and determination of the quantity of those substances. Means of isolation and separation of chemical classes by chemical or instrumental processes have been discussed. At this point, after separation of the individual components of the mixtures by gas chromatography, they must be identified and quantitated. Although a gas chromatograph can separate a complex mixture, GC retention times alone do not produce unequivocal identification of a substance. Identification of compounds by GC requires extensive use of standard compounds, usually with co-injection if a sufficient quantity of unknown material is available. Establishing identities of members of a complex mixture thus requires an extensive stock of standard compounds and the process is quite tedious and time-consuming if co-injection methods are used. As will be discussed below, quantitation from GC response alone can also be inadequate for complex mixtures.

If two components are not resolved chromatographically, it is impossible to obtain accurate quantitative data for either component. Most methods of quantitation require determination of a peak area and assessing the contribution of a single component to a peak multiplet is a difficult analytical problem. One instrument which can provide reliable and specific structural information and quantitative data for complex environmental mixtures is a mass spectrometer. In combination with the gas chromatograph, *i.e.*, GC/MS, it is an invaluable tool for environmental analyses.(1) The specific characteristics of the GC/MS which lend themselves to environmental analysis are: 1) low detection limit - generally on the order of low nanograms for identification and quantitation; 2) specificity - the mass spectrum of most compounds provides a fingerprint characteristic of an individual compound and data from which the structure can be deduced; and 3) quantitation - quantitative data can often be obtained even in the presence of unresolved components.

The combined GC/MS is well suited to computer interfacing and some quite sophisticated computer packages are commercially available. For complex mixtures, use of a computer in acquisition and manipulation of the data is a necessity. Scan cycles for a typical mass spectrometer interfaced to a gas chromatograph range from 1-5 seconds. Analysis times for complex mixtures may be 45 minutes to an hour or more, and collections of data incorporating hundreds or even thousands of mass spectra are not unusual. Extensive use of an analog system is simply not feasible on this scale of data acquisition and manipulation. The utility of the computer for subsequent processing of data is unquestioned: the computer can subtract background spectra, extract ion profiles of any given mass, reconstruct gas chromatograms at any requested amplification, plot mass spectra with any type of normalization desired, and produce tables of mass spectral data.

Although the mass spectrometer is well suited to environmental analyses, it is not a total panacea. Sensitivity limits with certain specific GC detectors are significantly lower. Many isomeric compounds give nearly identical mass spectra which makes specific isomer identification unreliable or impossible in many cases. Spectra obtained from the same compound on different instruments (especially magnetic sector instruments as opposed to quadrupoles) can differ significantly. The amount of data obtainable from a complex sample can be so great as to overwhelm the analyst. Lastly, the amount of data and the nature of the instrumentation itself require supervision by analysts with more than a minimal level of sophistication.

INSTRUMENTATION(2)

There are several criteria which GC/MS instrumentation must meet for the Master Analytical Scheme for organics in water (MAS). The goal of the Master Analytical Scheme is a total recovery for any compound of at least 40% and a detection limit of 0.01 μg/L as a lower limit. This translates to a sensitivity limit of 4 ng assuming a one liter sample size. The exact limit will be addressed by the Master Analytical Scheme. The GC must be able to accommodate a variety of columns, both packed and capillary. The GC also requires accurate control of oven programming, since analyses must be reproducible. Operating in the capillary mode requires modification of the injection system to either a split or splitless system, since capillary columns cannot accommodate the injection volumes which can be put on a packed column.

Mass Range and Resolution

Although the upper mass limit for most organic compounds of interest is about 500 daltons, the mass spectrometer must be capable of acquiring data up to approximately 1000 daltons since many derivatized species and brominated species have molecular weights approaching 1000 daltons. Of course, if the analyst is only interested in the application of this scheme to the lower molecular weight contaminants, a mass spectrometer with a more limited mass range can suffice. With the exception of residual gas analyzers, mass spectrometers with mass ranges more limited than 0-500 daltons are rare and unsuitable for this scheme. The resolution of the instrument must be such that the peaks in the upper mass range are resolvable. At a minimum, a resolution of 1000 at mass 1000 must be obtainable with the resolution being defined as the ratio of $M:\Delta M$ where M and $M + \Delta M$ are the m/z values of two adjacent peaks in the mass spectrum at a 10% valley. The sensitivity requirement, of course, applies simultaneously. If use of a more limited mass range is envisioned, resolution requirements are less restrictive but a minimum resolution equal to the maximum mass should be readily obtainable.

Data System

The data system, as a minimum, needs to be capable of spectral acquisition and processing, as well as generation of reconstructed gas chromatograms and selected ion plots. The system must also have the capacity for long-term data storage, for a variety of reasons. It is possible that a situation may arise in which many samples need to be analyzed in a short time interval and data processing must be delayed lest samples be lost. Also, a situation is readily envisioned in which a particular piece of information is sought at the time of the analysis but some other information is desired subsequently. In such a case, instead of reanalyzing the sample (in many instances, repeating an analysis may not be possible since additional sample may not be available), the data can be reexamined and the desired information extracted.

There are also features of a data system which would simplify the process of obtaining quantitative information. Quantitation requires extensive calculations, and the computer, properly programmed, can simplify or even completely execute these calculations.

Available Systems

Commercial GC/MS/DS systems are available from many manufacturers. A list of those companies currently manufacturing GC/MS/DS systems can be obtained from the readily available Analytical Chemistry Lab Guide and similar publications. In addition, independent data systems interfaceable to commercial mass spectrometers are also available and can be found in various lab guides. Complete GC/MS/DS systems cost from $100,000 - 250,000 depending on the sophistication of the system and the exact configuration requested.

The most commonly used commercial instruments can be divided into two categories, magnetic sector instruments and quadrupole instruments. A magnetic sector mass spectrometer separates charged particles according to mass because of the motion of these particles in a magnetic field: for a given field, different deflections are observed for particles of different mass, and different masses come into focus at the detector as the magnetic field is scanned. A quadrupole mass spectrometer separates charged particles according to mass because of the motion of these particles through coupled rf and dc fields: for a given voltage and frequency setting, the paths of particles of differing mass-to-charge ratios diverge, and as the frequency is scanned, different masses arrive at the detector. Traditionally, magnetic sector instruments have been more stable and less susceptible to spectral variations due to variations in tuning parameters.(3) Scan times have tended to be longer for magnetic sectors than quadrupoles since an electromagnet must be scanned and then driven to restart the scan cycle. However, recent magnetic sector instruments have scan cycles comparable to quadrupoles. Historically, quadrupole GC/MS/DS systems have been less stable than magnetic sectors, have exhibited mass discrimination in the upper end of the mass range, and have shown dramatic distortion of spectra acquired with alterations in tune. Quadrupoles easily lend themselves to selective ion monitoring (see below) since no variation in source conditions is required to shift from one ion to another.(2,3,4)

Detection Limits

Definitions used by commercial manufacturers to describe their instruments' detection limit specifications differ widely.(4) Although this unfortunate state of affairs has been discussed in great length at meetings of the American Society for Mass Spectrometry,(3) no standard definitions have been accepted by manufacturers (or mass spectrometrists). Definitions of detection limit vary from the very loosely worded, such as - "excellent spectra from 10 nanograms or less in most cases,"(4) through various modifiers such as the mass being detected,(4) signal-to-noise ratio,(4) column used,(4) etc. to specific statements of grams per second at a given signal-to-noise ratio for a specific ion of a specific compound at a given resolution.(4) It should be pointed out that, in comparing instrumental detection limits, resolution and method of introduction can have significant influence on the resulting numbers. When used in the selective ion monitoring mode [see below], sensitivity limits can be lowered by circa two orders of magnitude.

It must be pointed out that, if an instrument just meets the detection limits specifications for the Master Analytical Scheme under ideal conditions it may very well not meet them under actual laboratory operating conditions, and the detection limit is not expected to increase with age. Thus, if the envisioned quantitation is at the lower limits of the MAS, some effort should be expended on obtaining an instrument whose detection limits are well below those stated in the Master Analytical Scheme. On the other hand, if one envisions investigating only substances found in large amounts, sensitivity becomes not so important a criterion.

Resolution

Resolution is another instrumental parameter which is defined in different manners by different manufacturers.(4) Typical definitions are R(resolution) = $M/\Delta M$ where M is the mass and ΔM is the width of the peak at half height. An alternate definition for M and ΔM are M = mass and ΔM is the difference in mass between adjacent peaks. In this definition the resolution must be qualified by an indication of the separation of the two peaks, *e.g.*, height of the valley between the two ions, 10% or 50%. It should be pointed out that the resolution specified by manufacturers is often the maximum obtainable and that the sensitivity obtainable at that resolution is often very poor. The most realistic assessment of resolution is that resolution at which the instrument is typically run. For most GC/MS/DS work operating resolutions of around 500 are satisfactory although the ability to obtain a higher resolution when needed is obviously desirable. Quadrupoles generally state resolution as a function of mass range, i.e., resolution of 300 at mass 100. Comparisons of resolution vs. sensitivity as a function of mass under typical operating conditions between quadrupoles and magnetic sectors instruments have not been made.

GC/MS Interfaces and Scanning Rates

Since GC columns operate at a positive pressure while mass spectrometers operate in a vacuum, an interface (or separator) that removes the majority of the carrier gas without extensively depleting the organic content of the effluent is needed. There are three main types of molecular separators commercially available and in wide use: 1) membrane; 2) glass frit-Watson-Biemann; and 3) jet (glass or metal). A membrane separator can be of two types. The first consists of a Teflon® film through which helium diffuses preferentially. Peak distortion and time delays have been reported with this type of separator. The second type, a silicone membrane separator, utilizes the preferential passage of the organic material through a thin barrier to enrich the sample. Although high yield can be obtained by use of this separator, it suffers from some disadvantages: 1) extreme temperature dependence; 2) peak broadening; 3) low maximum temperature; and 4) possibility of membrane rupture.(2d) The Watson-Biemann type of separator consists of a sintered glass tube of ultrafine porosity enclosed in a vacuum envelope with flow restrictors at the entrance and exit. As the flow enters the sintered glass tube the pressure in the tube drops to about one torr. The carrier gas preferentially effuses through the glass and is pumped away. Several other materials, porous metal and ceramics, have been used in place of the sintered glass.(2d) The jet separator takes advantage of the different diffusion rates of different gases in an expanding supersonic jet stream. The effluent from the chromatograph passes through a restricted opening into an evacuated area between the first opening and a second orifice. The lighter carrier gas diffuses more rapidly than does the heavier effluent leaving the core of the jet stream enriched in the heavier effluent. This enriched core then enters the collecting orifice. The lighter gas is pumped away.(2d) Jet separators often consist of two jets in sequence (two-stage) or one jet (one-stage).

At least two modes of interfacing capillary columns to mass spectrometers are in use. Conceptually simplest is direct coupling of the column to the source. Since the flows through a capillary, 1-3mL/min, are such that the high vacuum pumping system can maintain an adequate source vacuum, these columns can be coupled directly to the source. Capillary column effluent is often, but not invariably, directed through a critical orifice in order to maintain positive pressure at the end of the column both to prolong column life and to preserve standard operating conditions. One can also connect a capillary GC column to a mass spectrometer via a molecular separator. Since separators operate at their highest enrichment efficiency at flows of 20-30 mL/min, some instruments add a make-up gas at the end of the capillary to bring the flow up to that found in packed columns and then pass the flow through a separator to lower the total flow to that which can be handled by the source pumping system.(4) Although direct coupling appears to be a simpler answer for interfacing capillaries, this aspect may be instrument-and operator-dependent.

Scan rates for commercial quadrupoles and magnetic sectors are quite closely comparable with 1 second scan times over a mass range of 1000 daltons being quite typical. With magnets capable of being rapidly driven to the scan starting point instead of being allowed to collapse at a slower rate, scan cycles for quadrupoles and magnetic sector instruments are quite comparable. Scan cycles of between 1 and 2 seconds (or less) over a range of 1000 daltons are quite typical. Such scan cycles are fast enough to be compatible with the finest capillaries available. Some caveats on scan speed should be noted. Some systems have achieved fast scans by taking only one data point per mass. Obviously, if that data point is not at the peak maximum, important quantitative information can be lost. Also, instrumental scan capability can be faster than arrival of ions at the detector. If ion statistics are poor because of arrival of too few ions at the detector, sensitivity will be poor.

Instrument Stability

Instrumental stability is another factor to consider in comparing GC/MS/DS systems. Stability encompasses both mass drift and changes in sensitivity between high and low masses. Obviously, the more often one must tune the mass spectrometer the less time available for analyses. In addition, the less stable an instrument, the more likely the data will be of poor quality and will not be reproducible over a given time interval.

Typical quadrupole specifications for new instruments claim stabilities of ±0.1 dalton through an 8 hour day.(4) Magnetic sector manufacturers normally do not specify mass stability although mass marker accuracy (often ± 0.3 dalton) is reported. No claims as to stability of focussing are made for quadrupole or magnetic sector instruments.(4) Some quadrupole systems have an automatic tune so that the mass spectrometer is tuned under computer control.(4) Some instrument manufacturers recommend mass calibration each day while for others mass stability over six month periods is common.(3,4)

Computer Software

Many manufacturers provide computer hardware and software packages.(4) All of these packages include the following capabilities: 1) generation of reconstructed gas chromatograms (*i. e.*, a plot of gas chromatographic peaks *vs.* a time or mass spectral scan number parameter); 2) generation of selected ion plots from full scan data in a convenient, stable, easily accessible medium (the computer extracts a profile of a given ion, tracking its rise and fall in intensity over all or some of the scans taken or elapsed time); 3) background subtraction (the user may select a background spectrum to be subtracted from any given spectrum or series of spectra, even the entire analysis, if desired); 4) storage of all scans from a run; and 5) hardcopy capability. Also, many instruments have realtime displays, simultaneous data acquisition and data processing and long term data storage (archiving), as well as computer control of the mass spectrometer.(4)

Most manufacturers supply library search systems with the software packages.(4) These search systems will be discussed in more detail later.

Types of Ionization Processes

The heart of any mass spectrometric technique is the ionization process. There are a number of ionization processes in use. However, only two are widely used in water analyses, i.e., electron impact ionization and chemical ionization.

Electron impact (EI) ionization is by far the most widely employed of the two forms of ionization. Approximately 95% of all mass spectrometry work has been done employing EI(2d,3) and it has been applied to all classes of compounds.(3). In this method, high energy electrons are emitted from a heated wire or filament. Interaction of the electron with substances eluting from the GC results in an electron being stripped from the eluent molecule forming a positive ion called the molecular ion. This positive ion often has a high internal energy as a result of the ionization process and fragments into smaller pieces. The molecular ion and fragment ions are extracted from the source and are separated according to their mass to charge ratio (m/z) by the magnetic or quadrupole fields.

The energy of the electrons formed from the filament is 70eV in normal operation. In many cases, however, lower ionizing energies are used. As the ionizing energy is lowered less energy is transferred to the molecular ion and, as a result, less fragmentation of the molecular ion occurs. At a specific ionizing energy, usually between 8 and 12 eV, no fragmentation occurs and only a molecular ion is observed. Thus, for compounds such as carbohydrate derivatives, steroids, and terpenes, which give only minute molecular ions, spectra at low ionizing energy can enhance the intensity of the molecular ion relative to fragment ions.(2cd,5) There are several drawbacks to this technique in that structural information obtained from the 70eV fragmentation pattern is lost. Also the best ionizing voltage to enhance the molecular ion is not always determinable beforehand, necessitating several analyses, and the absolute intensities are, at the lower ionizing energies, much reduced from the 70eV intensities. Filament lifetime can be greatly reduced by use at low ionizing energies. As a compromise, spectra are often obtained at 20eV where the fragmentation pattern may be less complicated than at 70eV but absolute intensities have not decreased drastically. In fact, some manufacturers routinely maintain the filament at 20eV between scans.(2d, 4) In this manner, the total ion current measured as the ions exit the source does not include the helium flow since 20eV is below the ionization potential of helium. One further disadvantage in use of low ionizing energies is that, for the most part, spectra contained in libraries have been obtained at 70eV and use of these libraries for identification is hampered.(2d) This disadvantage can be overcome by assembling a library of mass spectra of the compounds of interest obtained at 20eV by the analysts themselves.

Chemical ionization (CI) is a technique that has been used for some time in mass spectrometry as an alternative or complement to electron impact ionization. CI is a less energetic ionization technique, since the sample molecules are ionized by interaction with a reagent gas rather than by direct interaction with a beam of high-energy electrons. In CI, the reagent gas is introduced at relatively high pressure. Ionization of the gas in conjunction with the high pressure leads to ion molecule reactions, typically protonation. Methane is very commonly used as a reagent gas, and the following gas phase chemistry is observed:

$$CH_4 + e \rightarrow CH_4^{+\cdot} + 2e$$
$$CH_4^{+\cdot} \rightarrow CH_3^{+} + H^{\cdot}$$
$$CH_4^{+\cdot} + CH_4 \rightarrow CH_5^{+} + CH_3^{\cdot}$$
$$CH_3^{+} + CH_4 \rightarrow C_2H_5^{+} + H_2$$

Reaction with the effluent from the gas chromatograph yields protonated molecular ions. These protonated molecular ions were at one time called "quasi-molecular" ions. This term is not recommended.(6) The protonation reaction occurs with less energy transfer than does electron impact ionization and, thus, leads to less fragmentation and generally a more abundant molecular ion species (M+1 or M-1 from H_2 loss) than does electron impact. A textbook example of this is found in the mass spectrum of n-octadecane. The molecular ion under electron impact carries 0.5% of the ion current while the chemical ionization spectrum with methane as a reagent gas has as base peak the (M-1) ion which carries over 30% of the total ionization current.(7)

A variety of reagent gases have been employed in chemical ionization mass spectrometry. Gases most commonly in use are methane and isobutane.(8) Both gases react with the effluent to initially form protonated molecular ions. Protonation by isobutane is a less exothermic reaction (and transfers less energy) than protonation by methane, and thus leads to less fragmentation. Reagent gas background tends to be higher with isobutane than with methane.(3,9)

Methane and isobutane have been extensively investigated as reagent gases for a variety of compounds such as hydrocarbons, amino acids, alcohols, amines, ketones, esters, miscellaneous nitrogen compounds, carbohydrates, steroids, pesticides and organometallics [see, e.g., 2c].

Ammonia is another commonly used reagent gas. Ammonia can form protonated molecular ions or (M + 18) addition ions as a result of electrophilic attachment of the ammonium ion to the organic molecule; some clustering (i.e., $(M+(NH_3)_nH)^+$ is also observed. Very little energy is transferred in this reaction and, thus, ammonia chemical ionization leads to very little fragmentation. Ammonia also has been found to be very useful for selectively ionizing basic compounds such as amines, acids, esters, and alcohols in complex organic mixtures and for determining the molecular ion of polyhydroxylic compounds.(8) Ammonia, however, has not been systematically investigated for use as a reagent gas in all chemical classes. Nitric oxide is another reagent gas which has enjoyed some use although it, too, has not been systematically investigated as a reagent gas for all chemical classes. The dominant reactions with this reagent are hydride abstraction to form an M-1 ion and electrophilic addition to form $(M + NO)^+$ ions. This reagent gas reacts well with esters, acids, ketones, aldehydes, alcohols, and hydrocarbons.(8) It has been employed to differentiate between primary, secondary, and tertiary alcohols and to qualitatively assay components in complex hydrocarbon mixtures where attachment occurs with alkenes but not with cycloalkanes.(8) Argon/H_2O mixtures as a reagent gas have been used to mimic electron impact fragmentation while still enhancing a molecular ion species (usually M + 1).(8) As in the cases of NH_3 and NO, this mixture has not enjoyed wide use or investigation as a reagent gas for all chemical classes. Use of D_2O as a reagent gas has been shown to be useful in the determination of the number of active hydrogen atoms with the reactive hydrogen being replaced by deuterium.(8)

Since more of the total ion current is carried by a single ionic species under CI conditions than under El conditions, quantitation by single ion plots or by selective ion monitoring is easier and often more sensitive with CI than with EI.(9) These quantitation techniques will be described in detail in a later section.

Introduction of the reagent gas can be through a separate inlet line or the reagent gas can be used as the carrier gas for the GC. Most GC/MS/DS instrument manufacturers offer chemical ionization capabilities for their instruments.(4) The more recent instruments do not require extensive replumbing to change from electron impact to chemical ionization or vice-versa. In fact, changeover times of less than 30 seconds are normal.(4) Some manufacturers are offering simultaneous EI and CI operation by splitting the GC effluent into two separate sources - one operated in the CI mode and one in the EI mode.(4)

Although CI has been extensively used, especially in the biomedical field, it suffers from a lack of uniform operating parameters.(9) In addition to differences in spectra obtained with different reagent gases, variations in the pressure of the reagent gas in the source can lead to variations in spectra. Most mass spectrometers do not accurately measure source pressures and calculations of the pressure from the extent of ion-molecule reactions observed are rarely performed. In any case, no standard pressure has been agreed upon. Ion source temperature is another factor which can greatly influence the extent of fragmentation found in CI spectra. Also, although general CI reaction mechanisms can be predicted for classes or types of compounds, the exact nature of the reaction chemistry (i.e., observation of $M^{+\cdot}$, $(M+1)^+$, $(M-1)^+$, cluster ions, fragments, etc.) is not precisely known in advance. For this reason, CI sees its most valuable application as an adjunct or complement to EI techniques.(2) For example, if an EI spectrum of some material has been obtained, CI can often be used to confirm the assignment of the EI ion of highest mass as the molecular ion rather than a fragment.

Due to the lack of uniformity of operating parameters, minimal structural information provided due to decreased fragmentation, the tendency to be somewhat selective in its ionizing capabilities, and the sometimes unknown nature of the ion-molecule chemistry chemical ionization is envisioned as an auxiliary technique in water analysis rather than as the major mode of ionization.

The opposite sides of the coin from positive ion electron impact and chemical ionization mass spectrometry are the corresponding negative ion techniques.

Although negative ions have been examined by mass spectrometry for many years, negative ion mass spectrometry has not been generally accepted as an analytical technique due to the low yield of ions in most negative ion techniques. Negative ion mass spectrometry can be 10^3 less sensitive than positive ion mass spectrometry.

The recently developed technique of negative ion chemical ionization (NICI), however, has overcome the sensitivity problem for selected compounds. Negative chemical ionization has proven to be a selective method and, similar to electron capture gas chromatography, is most efficient for compounds with high electron affinities. The successful operation of the negative chemical ionization technique is dependent upon the production of a population of low energy (thermal) electrons in the ion source. These low energy electrons can then interact with molecules present in the source: (1) directly to produce negative ions by resonance capture of an electron ($M + e^- \rightarrow M^-$), dissociative resonance capture ($M\text{-}M' + e^- \rightarrow M^- + M'$ and/or $M'^- + M$), or ion pair production [$M\text{-}M' + e^- \rightarrow M^+ + M'^- + e^-$ (thermal) or $M^- + M'^+ + e^-$ (thermal)]; or (2) indirectly, by ionizing and reacting with a reagent gas present in the ion source to produce ions which interact chemically with the sample molecules (*e.g.*, addition of Cl^- or O^-, with possible subsequent further decomposition of the ionic complex thus formed).

R. Dougherty *et al.*(10-13) have made several important contributions to the study of the chemical processes involved in negative chemical ionization. In a study of the positive and negative isobutane chemical ionization mass spectra of twelve aromatic chlorinated pesticides, metabolites, and degradation products, the chemical ionization mass spectra were found to be considerably less complex than electron impact spectra, while the negative chemical ionization spectra with isobutane enhancement gas were exceptionally simple. The authors suggest that, because of the uncomplicated nature of the spectra, negative chemical ionization techniques should have considerable analytical utility. The various types of negative chemical ionization techniques have been applied to many types of compounds such as barbiturates,(14) chlorinated aromatics,(15) herbicides,(11) polycyclic chlorinated insecticides,(12) polycyclic aromatic compounds,(16) organophosphorus pesticides,(17) polycholorinated dibenzodioxins,(18) and aromatic chlorinated pesticides.(10)

In the majority of cases cited above, enhancement of sensitivity by a factor of 10^3 over positive chemical ionization techniques was often encountered. Since positive chemical ionization is usually a factor of 10 more sensitive than electron impact, negative chemical ionization mass spectrometry promises to be 10^4 times as sensitive as electron impact mass spectrometry for suitable compounds.

This technique requires extensive instrument modifications and several manufacturers offer these modifications. Costs vary from $4000 to $10,000 for the modifications. Magnetic sector instruments require means of reversal of the accelerating voltage, multiplier voltages, and magnetic current flow. The modification of quadrupole instruments requires some minor power supply changes and an offset multiplier with a collision surface. In addition the capability for rapid acquisition of alternate positive CI and NICI spectra is provided by one manufacturer.

Due to the selectivity of NICI the most probable applications lie in the area of detection of specific compound classes, e.g., halogenated compounds, rather than as a broad analytical technique.(3,10-18)

Field Ionization (FI) is an alternate ionization technique which also may be found to be useful in water analysis. Ionization occurs in a very strong electric field on the order of 10^7 to 10^8 volts/cm. Removal of an electron in this field occurs with a much smaller transfer of internal energy to the molecular ion than in the case of EI ionization. The FI technique, therefore, produces a high relative abundance of the molecular ion. Unfortunately, FI is approximately 10 to 100 times less sensitive than EI at the present time and for this reason and its lack of ready availability its routine use in water analysis is not envisioned.(2c,9)

High Resolution GC/High Resolution MS

One technique that does hold great promise for the future in this type of analytical program is that of high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).(19) In this technique, capillary columns are used in the GC to provide the separating power necessary to resolve the individual components of a complex mixture while the high resolution mass spectrometer provides absolute mass information and, thus, the elemental composition of the individual ions. Additionally, one can extract selected ion plots of a given elemental composition to determine whether compounds of given structural types are present. For example, instead of an SIP for 105 one can get an SIP for 105 of composition C_8H_9 and one for 105 of composition C_7H_5O. The tremendous amount of data that can be generated from an HRGC/HRMS run necessitates extensive computer capability and very sophisticated programs to extract and process data in reasonable and useful forms.

This technique, however, suffers from the long cycle times involved in obtaining a spectrum (ca. 10 sec) which defeats the high resolution capabilities of the capillary columns. At such time as the scan cycle times can be made compatible with capillary column peak widths, this technique should prove to be extremely useful.

IDENTIFICATION BY NON-COMPUTERIZED APPROACHES

Compound identification is one of the two crucial portions of the data reduction process, but it is the phase of the operation most often dismissed in the literature with the phrase, "The compounds were identified by mass spectrometry."(20-83) No mention is made of the criteria for identification, nor is any indication of the level of confidence in the identification given.

A compound identification can be made in several ways. Perhaps the simplest is a straightforward interpretation of the mass spectrum. This method can sometimes be used to arrive at the complete structure of an unknown, but in the case of a complex molecule, an identification based solely on the interpretation of the fragmentation pattern can give clues to the nature of the functional groups but may be in error regarding the complete structure of the molecule, particularly if the mass spectrum does not exhibit a molecular ion. Identification of mass spectra can also be based on comparison of the mass spectrum of the unknown with any of several published compendia of mass spectral data.(84-86) This can be done manually and, of course, can be combined with spectral interpretation. Even with comparison to literature, however, confirmation of identity can be uncertain.(2,87) Spectra in a compilation or library will often have been obtained on an instrument different from the one on which the spectrum of the unknown has been obtained. In routine operation there is usually an instrument-to-instrument variation in ion ratios observed in a given mass spectrum. Even on the same instrument at different times variations in the spectra are encountered. The variability between instruments is accentuated between instrument types, i.e., a magnetic sector instrument compared to a quadrupole.(3) Also, the exact spectrum obtained can be a function of the method of introduction of the compound of interest into the instrument.(3) The relative abundances of ions will be different for a mass spectrum scanned as a material is eluting from a direct insertion probe (at a relatively constant ion source pressure) vs. that same material eluting from a gas chromatographic column where ion source concentration of the material is constantly changing as it elutes.(2d,3) There is usually no information available with a compendium about the method of sample introduction or any history of the sample.(3) There is the further problem that the mass spectra of isomers often differ only slightly, if at all.(84-86) Alkyl benzenes of a given carbon number offer a prime example: mass spectra of o-, m-, and p-xylene cannot be distinguished. Sometimes isomers can be distinguished by elution times but often, as in the case of the xylenes where the m- and p-isomers co-elute even on 100 m of a SCOT column, elution times cannot unequivocally establish an identification. The best identification of a compound is based on comparison with a standard of authentic material chromatographed on the same column as the unknown with the mass spectrum taken on the same instrument.(3) However, in many cases (especially the higher hydrocarbon isomers) authentic standards for all isomers are not available.(3)

The EPA procedures for consent decree analysis(88) obviously stress identification and quantitation of a limited list of priority pollutants rather than total identification of all components in a sample. With respect to priority pollutants, identification is based on the predicted retention time of compounds of interest on a given chromatographic column, coupled with the observation of common maxima in as many as three ions of the mass spectrum. In the case of priority pollutant analysis, the question of criteria for identification of a total unknown is not addressed.

As indicated above, most identifications of compounds by mass spectrometry do not specify criteria for identification.(20-83) Priority pollutant analysis(88) does not require identification of compounds from their mass spectra but rather confirmation of the presence of a known compound. It is therefore essential to address the question of criteria for compound identification in the master scheme. These criteria could perhaps encompass several levels depending on time and materials available. At the first level would be a correspondence at some specified level between a given number of peaks in the literature mass spectrum and the unknown. A further bit of sophistication at this level would also include some criteria for correspondence of ion abundance measurements within a certain range. In cases where unknown and literature spectra are similar but do not fall within the specified limits, any compound identification would have to be considered tentative. At a second level of certainty in compound identification, use of the spectral correspondence criteria delineated above and superimposition of gas chromatographic retention times would constitute an unequivocal identification. The highest level of confirmation of identity would require comparison with an authentic material, a compound available commercially or possibly even specially synthesized. For many compounds of interest, mass spectral and retention window information has been acquired in analyses performed over the years in laboratories.(3)

Other Ionization Techniques

If ionization techniques other than standard 70 eV electron impact are used, identification of compounds from their spectra becomes a severe problem. No compendia of FI, CI, or NICI mass spectra exist. If they were to be compiled, there would not be agreement upon "a" spectrum of a compound under FI, CI, or NICI conditions. All of these techniques are subject to wide variations in spectral appearance as a function of experimental conditions, and there is no agreement on experimental conditions among mass spectrometrists. At present, the only reliable criterion for identification would be a spectrum of an authentic compound determined under exactly the same conditions as the unknown, and determination of all these standard spectra would be an extremely expensive and time-consuming process.

COMPUTER PROCESSING OF GC/MS DATA

Introduction

In recent years, there has been a very rapid development of automated techniques for the acquisition of mass spectral information. The methods for computer acquisition of mass spectrometry data were originally developed for high resolution mass spectrometry.(89-91) However, the application which turned out to have greatest long term significance was the technique of acquisition of mass spectral information from a gas chromatograph/mass spectrometer (GC/MS) operating in a continuously scanning mode.(92)

The first reports of this approach to automated GC/MS/DS data processing gave rise to a burst of activity by other researchers, and particularly by instrument manufacturers, to apply the continuous scanning principle to their own GC/MS/DS systems. As a result, thousands of laboratories throughout the world today have the capability of acquiring vast amounts of GC/MS data on dedicated small computers.(5)

In addition to the basic technique of continuous scanning mass spectrometry, a variation of the approach involving the gathering of mass spectral (MS) data for a limited number of ions has allowed enhancement of instrument sensitivity for the identification of specific compounds in gas chromatographic mixtures.(93,94) This technique, now called selective ion monitoring (SIM), is routinely available as part of most commercial gas chromatograph/mass spectrometer/computer (GC/MS/DS) systems.

The availability of on-line computer methods for data acquisition has given high hopes to those laboratories which are engaged in the solving of environmental problems, including water analysis, where unknown samples often contain hundreds of components. Whereas computer systems are capable of acquiring and storing over 3,000 mass spectra per hour during GC operation, the bulk of data generated has made it difficult to complete the analytical process. In this section, we will indicate some of the procedures which have been developed to help the analyst in this task.

Mass Spectral Processing Procedures

For the purposes of this review, the procedures available to the analyst for computer aid in the identification of unknown mass spectra will be divided into three categories. The first will be the description of basic methods of data acquisition and display, the second will address itself to the mathematical deconvolution of mass spectral data from extraneous information, and the third will be a description of the computer identification of unknown compounds from their mass spectra. These categories are not entirely discrete and independent. However, the information is organized in this manner to achieve greater clarity.

Many of the programs mentioned in this review are being used extensively by GC/MS/DS users throughout the world. Notwithstanding this fact, a critical evaluation of these procedures, based on appropriate control experiments, has not been published, particularly as these techniques apply to analysis of water samples. It should, therefore, be emphasized that although the programs mentioned are actually being used daily for practical analytical tasks, the entire field of automated mass spectral analysis must still be considered to be in the experimental stage, and the results derived from the use of such techniques cannot be classed as definitive.

Basic Computer Acquisition and Processing Methods

GC/MS instruments have been adapted to a wide variety of computer systems. The large majority of existing systems are commercial products which are either entirely supported by the mass spectrometer manufacturer, or by independent software firms who normally provide interfacing to the GC/MS instrument.(3,4) There also exist a number of independently developed and constructed systems based on a wide variety of data processors. The latter are primarily found in universities and in government.(3)

All of the systems have one feature in common; that is, they provide an interface which can sense the signal obtained by the mass spectrometer ion collector and convert it into digital form for storing in the computer memory. The original signal may be either digital if derived directly from an ion counter, or, more commonly, analog if derived from the output of the mass spectrometer's electron multiplier. In addition, interfaces frequently are constructed so that various functions of the mass spectrometer can be controlled by the computer.

The majority of computers associated with GC/MS systems are individual stand-alone computers, each dedicated to servicing a single mass spectrometer

These computers normally have small core memory (4K-32K) and usually are fitted with a variety of peripheral devices such as magnetic storage, incremental plotter, magnetic tape, etc. Other configurations also are possible. Some systems are built to service more than one mass spectrometer within a single central processing unit (CPU), while other approaches involve microprocessors or small CPU's which feed into a central master computer system.(3)

The computers are all capable of acquiring individual mass spectra from a GC/MS instrument operating in continuous scanning mode and storing spectral information on a bulk storage device, either a magnetic tape or a disk. For magnetically scanned instruments, the peaks are acquired with time or magnetic field used as a reference, and a subsequent step must be carried out to convert the raw mass position data into $\underline{m}/\underline{z}$ units. Newer magnetic systems, especially those equipped with microprocessors or independent CPU's, carry out the position to mass conversion in real time during the data acquisition process. Quadrupole data are normally obtained directly in mass converted form. Along with the observed mass, the raw mass spectral data contain intensity information derived either from an analog/digital converter or an ion counter which is part of the computer-GC/MS interface. Those systems which do not acquire the mass information during data acquisition time perform this process in a subsequent off-line operation.(3,4)

All of the newer computer systems now have improved software design, incorporating so-called "foreground/background" processing, which allows the application of multi-tasks through the computer system.(95) With these programs, data acquisition and processing can be undertaken simultaneously, and with the better designed systems, this doubling up of functions can be carried out without one procedure slowing down the other.

After the data are acquired, a variety of programs are usually available on each system to present the data to the analyst. A large number of options are available which can print out lists of masses and intensities for individual spectra, display usual mass spectrum bar graphs either on CRT computer terminals or incremental or electrostatic plotters, and provide plots of total ion current (TIC) as a function of spectrum number ("reconstructed gas chromatogram"). In addition, many systems can create graphs of individual ion intensities as a function of spectrum number ("single ion plots").

Some in-house software systems also provide software for obtaining quantitative data from GC/MS runs. This includes semiautomatic procedures to integrate individual ion intensities (either from full scan or MID data), create standard curves using a linear regression model, and reverse interpolation of unknown data from previously determined standard calibration runs.(3)

Methods to Improve the Quality of Mass Spectral Data by Deconvolution

Although the automatic recording of a continuous series of mass spectra acquired during a single gas chromatographic run represented a major breakthrough in technology, there still remained the task of analyzing and interpreting this vast array of data now available to the analyst. The approach first taken was the examination of the reconstructed gas chromatogram, followed by recall of individual spectra normally present at the tops of each chromatographic peak. These presumably represented the pure spectra of the individual components of each run. In many cases this procedure was very successful. When the signal-to-noise ratio was large and a component peak was unencumbered by closely spaced companions, identification by manual or computer methods was very successful. It was soon found, however, that in many instances the raw spectrum observed was not that of the pure component alone but contained additional peaks due to the presence of extraneous signals derived from a number of sources. These include low level, random electronic noise from the recording systems, extraneous peaks due to the presence of GC column bleed, low level impurities from the sample, and contributions from nearby peaks in the gas chromatogram which were not totally resolved by the column. A variety of more or less effective methods have been developed to try and remove these impurities by mathematical manipulation of the raw GC/MS data. Some of these methods will be described briefly.

Background Subtraction -- The technique of background subtraction is basically as follows: in its simplest form, a spectrum from either an unknown GC run or some blank run is chosen as a "background" spectrum. This spectrum is then numerically subtracted, peak for peak, from the unknowns within the run, and the resulting difference spectra are used for mass spectral identification.(3)

In a slightly more refined version of this technique, the background spectrum is determined manually by visual inspection of a raw TIC plot, and in some instances several background spectra are chosen for different ranges of the chromatogram.(3)

Another approach to deconvolution by background subtraction involves the subtraction of a portion of an adjacent peak which is identified as an impurity in an unknown. Frequently, the presence of such mixtures of unknowns can be detected by the analysis of the TIC plot for the run, since peaks containing mixtures of compounds are normally broader or less symmetrical than totally resolved components.(96)

The major difficulty associated with this approach is that background spectra are not constant, either qualitatively or quantitatively. Thus, what constitutes the background in one section of a run may be very different in another. As a result, it is difficult to design a computer algorithm for background subtraction in an automatic fashion. On the other hand, having programs which, by interaction with the user, can remove specific elements of background spectra may simplify the unknown spectra to the point where search programs or manual examination will allow the identification of unknown components.

Mass Max Analysis -- A second and more sophisticated approach to mass spectral deconvolution was published later by Biemann and coworkers.(97) This approach makes use of the principle that when a compound elutes from a GC column and is analyzed by continuously scanning MS, the ions of each component show maximum intensity at some mean elution time. The algorithm searches a GC/MS data file through each single ion trace for points of maximum intensity. The deconvoluted spectra are then defined as that collection of ions which have shown an intensity maximum within a given time window. This approach was designed to allow the separation of unknowns which are not sufficiently resolved to show individual TIC peaks, but which can be distinguished by the presence of single ion maxima which are not influenced by other ions not present in the particular unknown.

This idea is sound, and, within limits, has proved useful for the separation of multi-component mixtures in GC effluents. A major advantage of the system is that it is extremely rapid to execute and has been incorporated into several commercially available software processing systems.

The method seems to have some merits for the purpose of identifying the presence of unresolved multiplets. It cannot, however, always accurately predict actual spectra because of several deficiencies inherent in the technique. The major difficulty in this approach involves ions of the same mass which are present in several components of the convoluted mixture of spectra. The mass max procedure requires that an ion of particular mass be associated with one spectrum or another, and does not attempt to divide ion intensities among adjacent peaks. This often causes misidentification in computer search programs.

Peak Profile Analysis -- An algorithm for "cleaning up" mass spectra by this method was originally described by Rindfleisch and coworkers at Stanford.(98) This program is part of an integrated GC/MS data reduction system which runs on a PDP-11/20 computer. The program CLEANUP attempts to correct mathematically for spectral mixtures in three distinct ways corresponding to errors due to background noise and column bleed, signal saturation, and overlapping peaks. To do this, the program makes use of information both in advance and after a particular scan to distinguish between real peak unknown information and extraneous data. Individual ion intensity profiles are examined and corrected for the presence of constant or slowly changing background levels, random noise patterns, and the presence of overlapping multiplets. This is done by detailed analysis of the individual ion peak profile shape. The technique assumes that some of the ions will be essentially free of noise and other impurities, and their peak profiles can be used as models against which other peak profiles with more or less contamination are compared.

Using this approach, the CLEANUP program is capable of fairly sophisticated spectrum deconvolution and represents a very significant advance in the state of the art in this field.

Mass Spectral Searching

There are two philosophies which are used for the development of programs to identify the spectra of unknown compounds. The first, designated "heuristic methods", tries to develop a series of rules based on the mass spectral fragmentation patterns of known compounds, and by examination of the observed patterns in the unknown, identify the compound. The second, here called "library methods", seeks to identify unknown spectra by comparing them with individual members of a spectrum library of known compounds to determine the similarity between them. The heuristic methods have the advantage that they can, in principle, identify any compound, whether or not its mass spectrum has ever previously been recorded. The second approach, while limited to the identification of known compounds, is much easier to computerize, and constitutes the method by which the majority of automated searches are now being carried out. We will review some procedures of both types.

Heuristic Methods -- The most ambitious program for identification of mass spectra through the analysis of pathways of mass spectral fragmentation is being developed by a group of scientists at Stanford University headed by J. Lederberg as part of a program for the development of artificial intelligence.(99) This project has been fruitful in developing new ideas in computer simulation of human thought and has used mass spectral identification as one probe of the learning algorithm. Although this program may potentially outstrip all others in its ability to identify unknowns, it has not yet been made into an operational system.

Another heuristic method for mass spectral identification involving learning machines has been published.(100) Although the procedure is important as a tool in the development of identification algorithms, the technique has not yet evolved into a working method for the identification of broad classes of unknown compounds.

One method in this area which has shown distinct utility is the system developed at Cornell University known by the acronym Self Training Interpretive and Retrieval System (STIRS).(101) This procedure makes use of information which the user may know (such as molecular weight, presence of heteroelements, etc.) and combines it with commonly observed fragmentation patterns in a variety of compounds containing specific functional groups. By means of a series of "match factors", the program tries to evaluate fragmentations in the unknown against those of standard classes of compounds stored in its library. This is done in a very sophisticated manner, and allows the computer to identify compounds which in many cases are not present in any existing mass spectral library. Thus, for example, the STIRS program might identify a compound as being an aromatic amine, based on typical decomposition fragments of its molecular ion as well as on low molecular weight fragments characteristic for these kinds of compounds. STIRS, although by no means omniscient, may point the investigator to the identification of unknown spectra not previously recorded. The STIRS program is accessible on a national computer network and can be operated, at a fee, from teletype terminals remote from the central processor and connected via long distance telephone lines.

Library Search Programs -- A much more straightforward approach to identification of unknown mass spectra is the library search method. In this approach, an unknown spectrum is compared, sequentially, with the members of a stored spectrum library of unknown compounds. The algorithm for determining the goodness of fit varies from one method to another; however, in every case the final results are expressed as a correlation factor which usually is normalized so that a total mismatch will result in a match factor of 0.0 and a perfect identity between unknown and library member will show a match factor of 1.0.

There is some confusion regarding the significance of a given match factor. Most researchers are more interested in whether a particular search has yielded the correct compound than the quality of the correlation factor. Unfortunately, there is no simple way to correlate match factors with the correctness of the identification. The search program normally returns a small number of compounds in the library which were most similar to the unknown. If the library contains only one compound of a given class, then this compound would be reported for a variety of similar unknowns, even if the match factor were low, since no better fits were found in the library. It also frequently occurs that a highly impure spectrum is submitted to the search, and the identification is correct, even though the match factor is poor. Even high match factors do not assure correctness of identification, since frequently compounds of a given class may show similar spectral properties, and an unknown from this class may show a high correlation factor even though the identification is incorrect. Thus, the results of computer searching must be treated with considerable caution, and, in the last analysis, human judgment still plays an important role in this process.

There are a number of existing computer search programs available. Nearly every commercial GC/MS software system provides some type of search library and searching algorithm. Most of the algorithms are based on the method described by Hertz, Hites, and Biemann (Biemann search).(102) The system operates by choosing the two most intense peaks in each fourteen mass unit segment of the mass spectrum (a mass spectrometric "decade") for both the unknown spectrum and the library spectrum and applying a numeric factor to the search score, depending on the similarity of the intensities of these search peaks. The summed score for each decade within the mass spectrum is then normalized to yield a correlation factor for that particular match.

In addition to its residence on a number of proprietary systems developed by GC/MS software manufacturers, Biemann searching, along with two other methods, is now available as part of the NIH-EPA Chemical Information System.(103) These other programs are called probability based matching (PBM)(104) and mass spectral search systems (MSSS).(105) These systems operate under very different algorithms, but they all function similarly; namely, the operator types in mass and intensity data interactively with the computer, and he receives, within a few minutes, the computer search results for that specific unknown.

Incorporation of Retention Index Information into GC/MS Search Systems -- In addition to direct searching of unknown mass spectra from computer libraries, speed and quality of the search could be improved by incorporation of retention index information along with mass spectral data for the purpose of distinguishing compounds with similar mass spectra but having different retention characteristics on the gas chromatograph.(106) Two groups have recently reported on the incorporation of GC retention index information in conjunction with their search programs.(107,108) These features are written into the individual investigator's in-house computer system and are claimed to substantially improve the quality of their respective search algorithms. The programs have not been widely tested, and it is still premature to assess whether these particular methods will have general applicability for wide laboratory distribution. The chief problem in these systems is the difficulty in reproducing GC conditions sufficiently accurately to allow comparisons between laboratories. Nevertheless, it appears that the incorporation of retention index information into search systems represents a major step forward in the development of this important area of analytical research. This field is still under active investigation and improvements in techniques will undoubtedly be forthcoming.

QUANTITATION

Quantitation is the second crucial question that needs to be addressed by the Master Analytical Scheme. Once we have identified the organic components of a water sample, we must answer the question of the amount of this substance in the sample. As pointed out above, a lower detection limit for quantitation of approximately 4 ng is required by the master scheme. Several approaches to quantitation which meet this criterion have been taken by different groups differentiated in broad terms mainly by the types of mass spectral output utilized in the quantitation procedure. These specific approaches will be discussed in more detail in following sections. There are, however, several questions which have to be addressed regardless of the final quantitation approach taken. The precision and accuracy of a measurement are two very important parameters to be considered when quantitating a substance. The accuracy of a measurement defines how well one's results coincide with reality while the precision of a measurement defines the reproducibility of that measurement. Exact error limits for accuracy and precision cannot be given for quantitation by GC/MS/DS in broad terms since they vary with the approach used and with the matrix of the sample. These parameters will be discussed in more detail in the sections concerning the individual quantitation approaches. Suffice it to say that quantitation by GC/MS/DS can be extremely precise and extremely accurate barring errors introduced prior to GC/MS/DS analysis or operator errors in sample manipulation.

We have already discussed the problems encountered in the identification process in answering the question, "What defines positive identification?" This problem is again encountered in the quantitation process. Since many of the techniques used in quantitation can quantitate compounds at levels lower than that at which full scan spectra of a quality suitable for identification can be obtained, positive identification is a major problem which has to be addressed. This is further aggravated in cases where overlap with other components precludes obtaining acceptable spectra for identification. This is obviously an area that must be systematized in developing the master scheme. Approaches to answering this question will most likely involve retention windows, maximization of more than one significant peak within a given number of spectra and a minimum signal to noise level.

Whether to use internal or external standards is another question that is common to all quantitation approaches. Internal standards are compounds that were added at the initial step of the analysis and carried throughout the procedure. An external standard is usually defined as a standard added just prior to instrumental analysis. In some cases an external standard is a compound analyzed separately from the unknown mixture with an instrumental response of the two being compared. Use of internal standards produces the most accurate response since variations in laboratory procedures will affect both the unknowns and the standards. Use of both an internal and an external standard (first definition) would perhaps provide the most data since a measure of variations in laboratory procedures could be made by comparing the responses of the internal and external standards over a series of analyses.

In most cases and for the quantitation techniques which can be reasonably used in the MAS, a true external standard (definition two) cannot be used.

Once the type of standard to be used (internal or external) has been determined, then the identity of the standards must be decided upon. Obviously for internal standard use the compound in question should present a chemical behavior characteristic of its chemical class. The compound selected cannot be a compound that may appear in the water being analyzed. This limits the choice of standards to isotopically labeled compounds or esoterically substituted compounds such as polyfluorinated compounds. In addition, certain mass spectral criteria must be met. To avoid overlap of internal standard ions with ions from naturally occurring isotopes of any of the unlabeled compounds present in the original water sample there must be a minimum of three mass units difference, effectively eliminating carbon-13 isotopically labeled compounds from consideration as standards. The internal standard should obviously elute from the GC at a point different from that of any substance of identical mass, e.g., d_6-benzene (mass 84) should not elute in the same region as any of the hexenes (mass 84).**

**Compounds such as d_{10}-anthracene, perfluorobenzene, perfluorotoluene, octachloronaphthalene, decachlorobiphenyl, hexaethylbenzene, 1,2,3-trichloropropane, 2-bromo-1-chloropropane, 1,4-dichlorobutane and bromochloromethane are just some of the compounds that have been used as standards in water analysis.

Techniques for quantitation of compounds based on mass spectral data can be divided into categories depending upon the type of data used in quantitation. These categories are selective ion monitoring (SIM), total ion current (TIC) and selected ion plots (SIP).(109)

Selective ion monitoring (SIM) is a technique whereby only a selected few ions are monitored continuously as a function of time instead of scanning the complete spectrum.(9) Since, in a conventional scan, each mass is focussed on the collector for only a few milliseconds, the SIM technique, in which a given peak is monitored for the total elution time or significant fraction thereof depending on the number of peaks being monitored, will be much more sensitive for quantitation purposes - a factor of approximately 10^3 more sensitive. In addition to sensitivity, the increased time spent monitoring a given ion leads to greater precision. The monitoring of the selected ions is accomplished in different manners depending upon instrument type. In magnetic sector instruments the most common method is to keep the magnetic field constant while the accelerating voltage is varied to bring ions of different masses into focus. This process involves significant additional hardware and/or software and increases the cost of the system. In addition, alterations in source voltages, *i.e.*, accelerating voltage, cause changes in sensitivity and focus. Problems with drifting magnets and limited mass ranges that have hindered the use of SIM on magnetic instruments have been eliminated on newer instruments. Some manufacturers of magnetic sector instruments offer an option of changing accelerating voltage to bring different masses into focus or changing the magnetic field, leaving accelerating voltage constant. Changing the magnet does not, of course, affect focus conditions in the ion source but altering a magnetic field is slower than jumping a voltage. The magnetic field, once changed, also requires a small settling time. In some systems it is also possible to program sequences of ions to be monitored at different times throughout the chromatographic analysis. In quadrupole instruments the method of ion focussing is not changed, but rather than sweeping the voltages, the voltages are jumped between the values needed to focus the selected ions. Thus, no change in source conditions and therefore sensitivity is found except for the mass discrimination often observed in quadrupoles.(3,110) As in the case of magnetic sectors the voltage alterations can be controlled by hardware or software options and add to the cost of the system. It is very advantageous to have a system in which the actual peaks being monitored can be observed during the analysis. In this type of system one can ensure that the peak is being monitored at its maximum and that no drift is occurring in the mass spectrometer.

In SIM, a standard curve is customarily determined in which the instrument response of an ion of a compound of interest at a series of concentrations of this compound relative to a given concentration of the standard is measured. There has been some discussion of the relative merits of using peak height or peak area for quantitation. Most comparisons find little difference between the two methods and perhaps greater accuracy using peak heights where partially unresolved peaks are encountered.(9) Use of a linear standard curve assumes that the relationship between mole ratios and response ratios is constant. This may not always be the case due to several factors such as absorption of small amounts of a substance on glassware or on GC columns. An excellent review of the use of SIM and the determination of calibration curves which can be applicable to any quantitation method can be found in "Quantitative Mass Spectrometry" by B. J. Millard.(9) In general, the SIM technique is both the most accurate and precise method of GC/MS/DS quantitation. However, the very characteristics which make SIM the most precise and accurate technique also mitigate against its extensive application in quantitating the large number of compounds found in an environmental sample. Since relatively few ions can be monitored (and it would be desirable to observe at least two ions for any compound of interest to be confident of its identification), most species present are ignored and very little identification data are obtained. In addition, since the ions to be monitored must be designated before starting the analysis, SIM obviously is of little use in quantitating a totally unknown sample unless very limited and very specific information is desired. SIM can be very useful, however, in searching for and quantitating a limited number of known compounds.(111-119) Excellent results have been obtained in the analysis of specific compounds in water, *e.g.*, vinyl chloride,(117) tetrachlorodibenzo-*p*-dioxin,(115) insect growth regulators,(112) organohalides,(116,120), toxaphene,(121) and pesticides.(122) Some laboratories have used SIM to quantitate limited numbers of the consent decree pollutants.(3)

The second type of mass spectral data used for quantitation is the total ion current or TIC. A variation of this is the use of reconstructed gas chromatogram data. Quantitation in this manner is quite similar to the techniques which use GC detector response. In this technique, the total ion current due to a peak eluting from the GC column is measured. Most commonly, this response is measured against the response of known amounts of the compound although calibration curves as in SIM can be used.

The use of TIC for quantitation suffers from two serious if not fatal drawbacks for the purposes of the master scheme. The first drawback is that contaminants and background can contribute to the TIC peak intensity resulting in a loss of accuracy. The second flaw is that in complex mixtures, coelution of components is quite often encountered, rendering it impossible to ascertain which part of the peak intensity is assignable to which compound. These are flaws which quantitation by TIC has in common with GC/FID quantitation. The technique employing TIC data may find some use in analyses where the peak in question is sharp, well defined, well resolved and has a flat baseline. It is anticipated, however, that in most of the aqueous matrices of interest well-resolved chromatographic peaks will be the exception rather than the rule.

The technique of selected ion plots, SIP, also known as extracted ion current profile (EICP), uses a characteristic ion (or ions) of a compound extracted from full scan data to obtain quantitative data for the compound.(*e.g.*, 9,71,109,123,124,125,126) The response of this ion relative to the response of a characteristic ion from a standard is measured against the response of the same ion from a known quantity of the compound of interest relative to the same ion from the standard. Under ideal conditions, a calibration curve should be determined in the same manner as indicated for quantitation by SIM. Since this is not practicable when the analyst is attempting to obtain quantitative information about several hundred components of an unknown mixture, as is often the case in water analyses, several methods of using the SIP data for quantitation have been developed. One method is that of relative molar responses (RMR). The method of calculation of the RMR is as follows:

$$RMR_{\mathrm{unknown/standard}} = \frac{{}_{\mathrm{unk}} \qquad {}_{\mathrm{unk}}}{A_{\mathrm{std}}/\mathrm{Moles}_{\mathrm{std}}} = \frac{{}_{\mathrm{unk}} \qquad {}_{\mathrm{unk}} \quad {}_{\mathrm{std}}}{g_{\mathrm{unk}} \cdot A_{\mathrm{std}} \cdot GMW_{\mathrm{std}}}$$

where A = ion response, g = number of grams present and GMW = gram molecular weight. The value of the RMR is determined from at least five independent analyses. Thus in the sample analyzed:

$$g_{\mathrm{unk}} = \frac{A_{\mathrm{unk}} \quad GMW_{\mathrm{unk}} \quad g_{\mathrm{std}}}{A_{\mathrm{std}} \quad GMW_{\mathrm{std}} \quad RMR_{\mathrm{unk/std}}}$$

This approach assumes that the molar response is constant over the concentration range of interest. This point is one which must be addressed by the master scheme: what is the minimum number of points necessary to determine a response factor (or calibration line) which produces a 95% prediction interval? One report indicates a linear response from 10 ng/ul to 500 ng/ul for a variety of compounds.(127) Another similar quantitation method is measuring the response factor on a weight basis rather than on a molar basis. This method incorporates recovery data into the equation for the response factor: Relative Response Ratio (RRR) =

$$\frac{\text{(Peak area model)(nanograms marker)(marker recovery level)}}{\text{(Peak area marker)(nanograms model compound)(model recovery level)}}$$

Again, a minimum of five replicate analyses is used to determine the RRR.(3) Battelle Columbus Laboratories uses a similar equation in which the final number is given as ppb. Battelle measures their response factor at three different concentrations.(128)

The US EPA guidelines for the screening of industrial effluents for priority pollutants uses the SIP method also.(88) The response of an unknown is compared to the response of a reference standard which closely approximates the unknown response. The quantity of unknown is determined

$$\frac{\text{(Area of unknown)/(area for standard)}}{\text{Concentration of standard}(\mu g/L)} = \mu g/L \text{ of unknown}$$

Quantitation is also done by the internal standard method where response factors are calculated. The response ratio (R) is calculated as

$$R = \frac{Ac}{Aa} \quad \times \quad \frac{Ca}{Cc}$$

where Ac = area of characteristic ion from SIP for a known concentration Cc.

Aa and Ca are the corresponding values for the internal standard. R should be calculated for at least two concentrations, 40 ng and 400 ng.

The concentration of the unknown is calculated by:

$$c = \frac{Ac \times Ca}{Aa \times R}$$

where c = concentration of unknown. Ac is area of the SIP, R = response ratio, Aa is area of the SIP for the internal standard and Ca is the concentration of the internal standard. Laboratories following the EPA method have generally reported satisfaction with the quantitation procedures used.(3) Very complex environmental mixtures such as industrial effluents,(3,88) drinking water,(3,30,48,67,129) wastewater,(125,128) and energy related effluents(54,71) have been quantitated using this method. Error limits of ±10% to ±50% have been associated with quantitation by SIP's.(3,128) The people using this method in its several variations, although realizing its imprecision relative to SIM, express satisfaction with the results obtained.(3)

In order to use selected ion plots for quantitation with a reasonable degree of precision, one must obtain a sufficient number of data points in scanning over the chromatographic peak as it elutes. If the instrumental scan cycle is too slow, data taken for replicate samples will exhibit very poor precision. The question of what constitutes a sufficient number of data points (and, thus, a sufficiently rapid instrumental scan cycle) will be addressed in the master scheme. A workable compromise between the scan cycle capabilities of some of the instruments (one second per cycle or possibly even faster) and the acquisition of a reasonable and workable amount of data with good statistics for arrival of ions at the detector will have to be reached. From the point of view of quantities of data generated, one would desire to use a scan cycle time no faster than necessary. The scan cycle time required to produce an acceptable number of data points over a chromatographic peak will vary with the type of column used: faster cycles will be required for the sharp (10-15 seconds) peaks eluting from a capillary column than for the broader peaks observed from a packed column. The question must be addressed and resolved in each case.

Mass spectrometric techniques which enhance the intensities of ions characteristic of a compound at the expense of less informative ions for a given quantity of compound can prove quite useful in quantitation. The increased ion intensity permits the lowering of the detection limit which is a very useful factor. As pointed out above, one technique that can enhance the intensity of a characteristic ion is chemical ionization. CI may, therefore, be quite useful in the quantitation of specific compounds and the master scheme should address this possibility, especially with compounds having poor EI mass spectral reponse. It must be remembered, though, that no matter which method of quantitation is employed, new calibration curves and/or response factors must be determined for every different method. The question of stability of calibration curves and response factors must also be addressed. How much do these parameters change with instrumental changes (*i.e.*, changing a filament, cleaning a source) and with time? Appropriate experiments must be done to provide answers to these questions.

Ionization Techniques Applied to Quantitation

Electron impact, since it has been applied in the identification of all compounds, is applicable for the quantitation of all compounds. In many instances, however, other techniques may offer advantages for quantitation. This is especially true of compounds which, under electron impact, do not give characteristic higher mass ions of reasonable intensity. Although the low mass ions may have excellent intensity for quantitation, these lower mass ions are usually quite nonspecific and errors can occur in quantitative assessments even in conjunction with GC retention data.

Chemical ionization has often proven to be an extremely useful ionization mode in conjunction with quantitation. This is due to the fact that, although EI normally produces a slightly greater total ion current from a given sample, CI can produce ions of high molecular weight, usually some molecular ion addition species, that carries a greater proportion of the total ion current than does EI. CI has been used extensively in biomedical applications in conjunction with SIM with low picogram levels of drugs being quantitated and in some cases femtogram quantities.(19) No systematic application of CI to the quantitation of trace organic constituents in water samples has been reported.

Quantitation in conjunction with CI could be, a priori, applied to any chemical class. It would be expected, however, that a substantial advantage to using the technique would be realized in those circumstances where conventional EI sensitivity is low. Such is the case of compound classes which do not exhibit molecular ions of reasonable intensity or those situations where ion current is diffused by extensive fragmentation under EI. In comparison, CI can produce a molecular ion species carrying a much greater percentage of the total ion current.

CI is most likely to be of benefit for those classes of compounds with polar functionalities, i.e., most amenable to proton transfer, such as alcohols, amino acids, nitrogen-containing compounds, alcohols, ketones, aldehydes, and esters.(2c) Utility of CI would be anticipated to be marginal for hydrocarbons and halogenated hydrocarbons. Since systematic applications of CI quantitation to the analysis of the chemical classes (as defined in the work statement) in water samples have not been reported, the master scheme should address the possibility. It must be kept in mind, however, that it may not prove possible to isolate those classes amenable to CI quantitation by themselves. This will tend to mitigate against the use of CI for quantitation. Additionally, in those laboratories not equipped for CI capability or in which the changeover from EI to CI is a laborious, time-consuming process, extensive use of CI may face a great activation barrier.

Negative ion chemical ionization has not been applied to the quantitation of aqueous trace constituents. Since the technique is similar to electron capture, quantitation using NICI may prove to be advantageous when applied to extensively halogenated compounds. Reports of quantitation by NICI of halogenated and phosphorus-containing compounds indicate an enhancement factor of 10^3 and greater for NICI in comparison to EICI.(17,18) The relative unavailability of NICI instrumentation and standardization mitigate against its use in the master scheme except as a last resort.

Field ionization has not been applied to environmental quantitation and, in fact, few references have been made to GC/MS/FI.(130,131) At a time when the technique of GC/MS/FI has been worked out, investigation of its use in environmental quantitation may prove beneficial. At the present time, FI may be considered to be outside the scope of the master scheme.

It must be remembered, though, that no matter which method of quantitation is employed, new calibration curves and/or response factors must be determined for every different method. The question of stability of calibration curves and response factors must also be addressed. How much do these parameters change with instrumental changes (*i.e.*, changing a filament, cleaning a source) and with time? Appropriate experiments must be done to provide answers to these questions.

QUALITY CONTROL

The level of confidence which can ultimately be reposed in the quantitative data generated for organic constituents in various types of water is directly related to the stringency of the quality control measures imposed and the degree of faithfulness with which they are followed. The gas chromatograph, mass spectrometer, the interface between the gas chromatograph and mass spectrometer, the computer, and subsequent data handling procedures all require that strict quality control be exercised to assure that numbers generated will be both accurate and consistent, both between laboratories, if interlaboratory coordination of procedures and data is attempted, and within a given laboratory over a period of time (*i.e.*, replicate determinations over a period of time on identical samples give identical results). In many cases in the reported literature, a significant criticism can be made of the reporting of levels of trace organics in water samples without reporting appropriate analytical quality assurance. In many cases, quality assurance measures are not reported simply because no quality assurance was done. In some instances, quality control measures have been taken but the analysts have not reported the nature or extent of the measures taken. Very often, the response to a question on quality control measures is that a blank was run or a spiked sample was analyzed.(3) What is required in the area of quality control in GC/MS/DS analysis of trace organic constituents of aqueous samples is a logical and thorough program which carries through every stage of the analysis from the acquisition of the samples to the reporting of data.

The first essential of a quality assurance program is the maintenance of accurate records. It is vital for the success of the programs that the entire history of a sample from its acquisition or receipt to ultimate generation of data be known. Logging of the progress of the sample at every stage is vital; when data are archived, rapid retrieval (and thus accurate sample logging) is essential. Without clear records, data can be lost or improperly handled. In some cases, loss of data would merely necessitate repeating the sample analysis. In other cases, an entire sample workup might have to be repeated. In still other instances, a sample might be totally irreplaceable. Thus, the basis of a good quality control program is total accountability for both the samples themselves and the data.

In order to obtain good results, it is necessary that all the instrumentation be operating properly. Since, in order to compare results between laboratories or in the same laboratory over time intervals, it is essential that the exact state of the system and each of its components be accurately known, these must be checked frequently. Gas chromatographic columns differ in separating properties because of a variety of factors. The parameters usually reported in the literature for a given analysis by gas chromatography include the material of which the column is made (usually glass, stainless steel, or sometimes nickel), its inner diameter (typically 1/4" or 1/8" for a packed column, often not specified for a capillary), phase and loading (i.e., 2% OV-17), support (i.e., Chrom W-HP), length of the column, type of capillary (SCOT or WCOT), and operating conditions (e.g., 20-240°C @ 8°/min). Carrier gas and flow are often but not invariably reported. There are several parameters which are not routinely stated or defined which can affect the success of the analysis: quality of column packing can vary drastically; supposedly equivalent packing made in one laboratory can differ greatly in separating properties from packing supplied by a commercial source; successive batches of packing from the same source can vary; and properties of the same column alter and deteriorate with age. It is vital for a quality control program (and for uniformity of analytical data generated) that quality control measures pertaining to the gas chromatograph be instituted and followed. For a given analysis, a standard column(s) must be defined and this column(s) must be required to meet performance specifications such as number of theoretical plates and performance upon analysis of some standard reference compound or (more probably) mixture of compounds. Acceptable limits of performance will need to be defined and columns which do not meet those criteria because of deterioration or quality of packing or quality of coating in the case of capillaries must be discarded. Several means of testing columns are in use. A mixture of cholestane and testosterone has been used to test inertness of packed columns in our laboratories. For capillary columns, a solution containing equal amounts of a phenol derivative and an aniline derivative is often used to test for acidity or basicity while polar compounds such as decylaldehyde and decanol are used to test for polarity. The exact nature of these performance criteria for gas chromatographic columns must be defined during the initial phases of the master scheme.

Parameters which will need to be specified include the exact nature of the test mixture or, indeed, if different mixtures will be used for different analyses, as well as number and concentrations of specific compounds. A standard method of preparation for the standard solutions must also be specified. Exact operating conditions for the analysis of these mixtures must also be specified. The frequency with which the analysis of standards must be performed will also need to be specified, i.e., must the condition of the column be checked daily (or even more often), weekly, or possibly as infrequently as monthly. All of the information generated in the course of monitoring column performance must be accurately entered in an up-to-date log of performance so that the exact condition of the column at any given time is a matter of record.

Another system variable which must be assessed is the operation of the separator, if a separator is used. Very frequently (but not invariably) the type and operating temperature of the separator are reported in the literature. An appropriate choice of components for the standard mixture will insure that proper cognizance is taken of the state of inertness of the separator system (i.e., separator plus transfer line to the mass spectrometer). Since, in most instances, the column itself can be evaluated on a GC which is not coupled to a mass spectrometer, repeating the analysis on the coupled system also provides a check on the condition of the separator/ transfer line. Currently, some groups are using the ratio of M^+ to $(M-18)^+$ in cholesterol as compared to the same ratio obtained by direct insertion to test the inertness of the separator and transfer lines since thermal loss of water from cholesterol is a facile process. Other groups are using the peak shape of methyl stearate as a test for inertness. Any tailing observed can be attributed to problems with the separator.

Quality control measures for the mass spectrometer present a wide range of problems. Many factors influence the operation of a mass spectrometer and thus affect the ultimate quality of the analytical data generated. One variable is sensitivity: as discussed in the section on instrumentation, even a definition on which all instrument manufacturers and users can agree has not been set forth. Age of filament, cleanliness of source, cleanliness of rods for a quadrupole, age and/or quality of a multiplier all affect sensitivity, and all are difficult to define precisely. Some definition of mass spectrometer (or system) sensitivity will need to be made for purposes of the analysis of organic components of aqueous samples. This may take the form of a specification of a signal-to-noise ratio for signal generated by a given quantity of a standard material on-column, or some other assessment of amount of signal for a specified amount of material. Again, an operational/ performance definition will be required, since there is currently no standard definition acceptable to all mass spectrometrists.

Another parameter which has a great effect on system operation is the tuning of the mass spectrometer. The tuning of a mass spectrometer affects mass assignments of peaks (referred to as calibration of the system), ratios of abundances of ions observed in the mass spectrum, and shapes of the mass spectrometric peaks, especially in the case of quadrupole mass spectrometers. Identification of compounds is often based on comparison with standard compendia of mass spectral data(84-86) and a correct identification requires that the spectrum of the unknown recognizably corresponds to the spectrum of the reference compound. The tuning of the system also affects the mass spectrometric peak resolution, or the ability to resolve a peak from the adjacent peaks one mass unit removed. Poor resolution can result in the data system's interpreting a broad peak as a multiplet, with subsequent distortion in the ion abundance ratios and possible uncertainties in spectral interpretation. In recognition of these problems, at least one attempt has been made(132) to select a test compound and a set of tuning conditions which would facilitate intersystem standardization. The compound chosen in this study was decafluorotriphenylphosphine (DFTPP) and relative ion abundance criteria were set which could be met by suitable adjustment of system tuning parameters. The ion abundance criteria set down for this compound are presented in Table 1. The $(M^+ + 1)/M^+$ ratio was set as .20 ± .03. The m/z 200 to m/z 199 ratio should be .07 ± .02 and the m/z 70 to m/z 69 ratio should be 0.02. It was reported that use of this compound and the specified

Table 1. ION ABUNDANCE CRITERIA FOR DECAFLUOROTRIPHENYL PHOSPHINE (DFTPP)

m/z	Intensity(%)[a]	m/z
51	30-60	198
68	<2	69
70	<	69
127	40-60	198
197	<1	198
198	Base Peak	
199	5-9	198
275	10-30	198
365	1	198
419	Less than	443
442	<40	198
443	17-23	442

[a] Read: e.g., m/z 51 must be of intensity between 30 and 60% of m/z 198.

criteria provided a reasonable basis for comparing output for a wide variety of GC/MS/DS systems.

It is informative to note that in a comparison of DFTPP spectra run on four magnetic sector instruments and six quadrupoles prior to outlining the tune criteria, the magnetic sectors had very similar spectra, e.g., the molecular ion varied from 80-100% while for 11 quadrupoles the ion varied from 2.5 to 100%.(132) Obviously there was a great need for standardization of operating parameters. It has been reported that even when tuning a quadrupole to the specifications of Budde et al., variation in relative abundances of internal standard ions (m/z 55 and m/z 128) for the same amount injected varied as much as 1:1 to 4:1.(3) Since the internal standard ions occurred in different tuning regions of the quadrupole mass spectrometer and the acceptable ranges for ion intensities in these regions relative to the molecular ion are rather broad (m/z 51 can be 30-60% of mass 198 while m/z 127 can be 40 to 60% of mass 198), this problem is not totally unexpected. Various other compounds have also been used. A study in 1973(133) used n-hexadecane and 1-phenylundecane. Several participating laboratories used both quadrupole and magnetic sector instruments to obtain mass spectra of these compounds. Ion abundance measurements agreed reasonably well below mass 100 but varied quite widely above this mass for a variety of reasons. Some common mass spectral system calibrants are perfluorokerosene and perfluorotributylamine but both of these compounds lack peaks of reasonable relative abundance in the high mass regions. Perfluorodecalin has been suggested as a test compound(134) but also lacks abundant ions in the higher mass ranges. The family of fluorinated alkyl s-triazines is often proposed for use as standard reference materials but the mass spectra of these compounds exhibit domination by the ion of mass 69; there are also extensive regions of the spectrum where no peak appears. Another compound which has been used to calibrate ion abundance ratios is triphenylnaphthalene.(136)

Since DFTPP is in extensive use within the Environmental Protection Agency as a system calibrant,(3) use of this compound will be evaluated. This compound and/or others will ultimately be used as the compound of choice for standardization of the mass spectral systems. It will be necessary to specify limits on the range of relative ion abundances in order to achieve a satisfactory level of inter-system standardization.

It is anticipated that, as part of a quality control program, reagent blanks will be analyzed regularly, and records of these analyses will be maintained permanently to support the validity of the data. The results will prove that good control was exercised at all stages of the analytical procedure and define precisely the level of background that was beyond control. Frequent or occasional analysis of spiked samples is also valuable in establishing that a given compound, if present in the matrix, could be detected and/or identified at a certain level. Usually when any quality control measures are reported in the literature, use of blanks or spiked samples is the means employed.(3) These are necessary but not sufficient for an analytical quality assurance program.

If other ionization techniques are employed in the mass spectral analysis of trace organic constituents of aqueous samples, quality control measures must be instituted to ensure intersystem standardization. Since both field ionization and negative ion chemical ionization are presently at the frontiers of developmental research, definition of standard parameters between two scientists doing research in these areas is still very much an area of disagreement. For these ionization techniques, no uniform, universally acceptable sets of experimental conditions have been established. Indeed, it is possible that experimental conditions may be unique to the mass spectrometer employed. Also, at present a high level of professional expertise and experience is required to obtain favorable results from the use of FI and NICI. For these reasons, extensive use of these ionization techniques in the master scheme is not anticipated.

Standard positive ion chemical ionization is subject to some of the same constraints enumerated above. It has been a subject for debate at meetings of the American Society for Mass Spectrometry for many years to decide just what to consider "standard" chemical ionization conditions. There is no universally acceptable set of conditions (both source temperature and gas pressure have a profound effect on the nature of the chemical ionization mass spectrum) for obtaining a methane chemical ionization mass spectrum nor any agreement on what "the" methane CI spectrum of a given compound is. Faced with these constraints use of CI with adequate quality control so that intersystem standardization is possible becomes quite difficult. Conditions of source temperature and gas pressure will need to be defined on at least two systems and the degree of correspondence of resulting spectra assessed in order to evaluate the utility of CI techniques for the master scheme.

RECENT DEVELOPMENTS IN THE APPLICATION OF GC/MS TO WATER ANALYSIS

Interest and activity in a field of research or application can be gauged by the frequency with which developments are reviewed. By this criterion, application of GC/MS/DS techniques to the analysis of aqueous matrices must be at an all-time high, with no indication that interest in the use of the combined technique is waning. Use of purge and trap methods for the analysis of very volatile constituents of aqueous samples has been reviewed,(137) and recent modifications in purge and trap procedures recommended by the Environmental Protection Agency have also been reviewed.(138) The application of GC/MS/DS to the qualitative and quantitative analysis of organic water pollutants has been reviewed several times,(139-142) and recent reviews have also stressed the value of capillary gas chromatography coupled with automated data handling techniques(143) and accumulation of spectral reference data for organic trace pollutants in water.(144)

A rapidly expanding area of research is the application of computers to the analysis of water pollutant data. A case in point is the continuing development of the Water DROP program.(145) The function of this computer program is to provide a comprehensive list of organic pollutants which have been found in water, so that the database could be searched by country, state, or city, as well as water type. Representative fields for searching would include water type, sampling date and location, concentration, identification method, indication of confirmation of identification, chemical information, literature reference, and several others. The database has been designed for ease of searching and updating, and has its foundation in a list published in December 1976 by Shackelford and Keith.(146) The Water DROP database is publicly available as a part of the NIH/EPA Chemical Information System, and the database is continually being expanded.

A further development in the use of computers is the automation of GC/MS data reduction. Instrument manufacturers have attempted to use their computerized systems to their full capability to make data reduction fast, efficient, and cost-effective. Most GC/MS/DS now sold allow positive identification of compounds of interest by comparison with a library of known spectra (using either forward or reverse search, according to user preference) and automatic quantitation by comparing responses for compounds of interest to responses of standards. Some systems will allow comparison of relative retention times to add confidence to the identification.(147-151)

A goal for automated data analysis has been the development of a computer system to evaluate the data as an experienced human would, using computer assistance. An extensive program to perform this type of analysis has been developed and consists of four basic parts:(152) 1) a program to locate and identify the standard in every set of GC/MS data; 2) a program to find and extract the spectra of components observed in the GC/MS analysis;(153) 3) a spectrum matching system to allow identification of components;(154) and 4) a program to collate and report results. Data obtained from the application of this program to analysis of aqueous industrial effluent extracts show that the automated techniques are at least equal to manual techniques for pointing out components and identifying these components by spectrum matching with a reference library.(152) However, the more convoluted the chromatographic analysis, the more difficulty the automated system encounters because of overlap of common ions and problems with peak shape and the ability to distinguish one chromatographic peak from another where there is extensive overlap in elution. Probability calculations on co-elution show, for example, that a two hundred component mixture will, on the average, have 20% of the components occurring in the form of multiplets, even with the use of capillary columns.(155) In practice, the occurrence of multicomponent multiplets may be substantially worse because of the presence of a large number of closely related (and, therefore, closely spaced in elution) isomers. There would thus be a theoretical limit for the effectiveness of automated methods of GC/MS data analysis when component identifications are made by direct search against a reference library.(155)

Computerized automated quantitation procedures can provide a great savings in time for the analyst, and are very cost-effective where an in-house computer can be used to do a reverse library search of a library of standard compounds to provide qualitative analysis. The library can contain user-generated reference spectra, relative retention times (as an additional reference for accurate identification), response factors (to allow quantitative calculations), and selected quantitation masses for a number of compounds of interest.(156) In a study featuring Grob Closed Loop Stripping Analysis with capillary GC/MS/DS, statistical analyses were performed on relative retention times, gas chromatographic peak areas, response factors, amounts, and recoveries observed under conditions of replicate analysis. Relative retention times showed excellent reproducibility (±0.7% of the average value), response factors varied from ±3.3% to ±14.2% of the average values (with some effect on response factors due to the abundance of the ion selected for use in quantitation), gas chromatographic peak areas varied on an average of ±13%, with amounts varying an average of ±9%.(156) Using an internal standard for quantitation compensated for these changes. Computerized automatic quantitation requires accurate library spectra and reproducible relative retention times and response factors. Close reproducibility of retention times allows the automated procedures to use narrow search windows which should result in greater success in distinguishing isomers which elute in close proximity. Compound recoveries vary over a wide range, depending on the nature of the compounds, differences in water solubility, and vapor pressure of the compound.(156) Error in determination of low nanogram response factors has been found to be analyte-dependent: compounds similar to the internal standard used (anthracene-d_{10}) show relative standard deviations for single-level response factors of approximately 1.2%, while compounds different from the standard in chemical and physical properties can be determined with a relative standard deviation <20% over the short term.(157)

Fused silica capillary columns have been and are being extensively used in environmental analysis. Chromatographic data have been found to exhibit excellent relative retention time precision. Excellent interlaboratory accuracy are reported when multiple internal standards are used to bracket the chromatographic elution range.(158) A relative standard deviation generally <10% at 50 ng for response factors of most of the compounds of interest over the long term indicated good precision of determination.(158) An Environmental Protection Agency manual defining the areas of applicability of GC/MS in environmental analysis has been prepared.(159) The manual describes preparation of environmental samples by methods specifically tailored to the requirements of the GC/MS technique, processing and interpretation of data, procedures for quality assurance/quality control, techniques for quantitative analysis of GC/MS data, requirements for software to perform qualitative and quantitative analysis, recommendations for preventive maintenance of the GC/MS/DS, a guide for troubleshooting in the GC/MS/DS, and a bibliography.

In contrast to the Master Analytical Scheme, which aims to develop a broadbased method applicable to all chromatographable organic materials in water, specialized schemes for single compounds or single chemical classes are being developed to meet specific needs. Methods have been developed to apply GC/MS/DS to the analysis of nitrophenol isomers in fresh water and ocean sediments,(160) pentachlorophenol in water,(161) and to the distribution of alkylnaphthalene isomers in complex groundwater or chemical spill samples.(162)

GC/MS/DS has been used to identify fluorocarbons in the lower Main River,(163) and to compare data obtained by use of DuPont and LKB instrumentation in the analysis of organic contaminants in water.(164) When sampling and enrichment conditions were comparable, results were satisfactory on both systems; differences in performance were seen chiefly in the comparison of capillary and packed column chromatography, with more unambiguous identifications for components of complex mixtures being observed in the capillary mode. Trace amounts of organic materials in tap water were detected by GC/MS/DS to assess the health hazard in drinking water.(165) Trace organics in tap water, river water, seawater, rain water, sewage and sediment were characterized by GC/MS/DS,(166) and a gas phase stripping technique has been described for the concentration and subsequent measurement of trace quantities of volatile organic compounds in water by GC/MS/DS.(167) Analysis by glass capillary GC/MS/DS is the final step for identification, confirmation, and quantification of individual organic compounds isolated from drinking water concentrates and advanced waste treatment water concentrates following extraction of the concentrate into acidic, basic, and neutral fractions.(168) Low-boiling organic compounds in tap water have been adsorbed on Amberlite XAD-4, then eluted and identified by GC/MS/DS.(169) A semiquantitative method for determining trace organic compounds in raw and treated surface water, groundwater, and industrial wastewater uses purge and trap techniques for isolation of volatile components, with subsequent GC/MS/DS analysis.(170) Trace organic compounds in Philadelphia drinking water were characterized by GC/MS over a two-year period.(171) Wastewater and water purification plant effluents from chemical and pharmaceutical plants were analyzed by capillary

GC/MS and found to contain volatile nitrosamines.(172) Computerized GC/MS has been applied to other problems in water pollution: a chemical plant wastewater containing organic compounds was discharged into a city sewer, mixed with other industrial effluents, and was ultimately treated in a Philadelphia plant using classical secondary methods. Treated effluent was discharged into the Delaware River; during high tides the treated effluent was carried upstream where it was able to enter the city drinking water treatment plant. GC/MS/DS analysis of the water at various stages showed that concentrations of chemical pollutants were reduced by dilution but not by the water treatment methods employed.(173) Industrial organic compounds in wastewater, river water, and sediment were identified using MS (electron impact, methane chemical ionization, high resolution MS), as well as gas and high pressure liquid chromatography.(174) When GC and GC/MS/DS results for priority pollutant analysis were compared in the characterization of selected surface waters, industrial wastewaters from coal-fired boiler facilities, and wastewaters from chemical processing industries, sensitivities by GC were found to be in low ppb to sub-ppb levels, while GC/MS/DS sensitivities were at the 1-10 pg level (low ppt range) for many samples.(175)

Trace organic constituents of raw and potable waters were quantified using GC/MS/DS with deuterated internal standards, with the best precision of measurement obtained with peaks appreciably above the detection limit.(176) The presence and behavior of organic pollutants in an aqueous environment surrounded by an industrialized area were explored using capillary GC/MS/DS.(177) Trace organic components of tap water were extracted using an Amberlite XAD-2 resin column and identified and quantified using GC/MS/DS techniques.(178) GC/MS/DS has been applied to the characterization of organic constituents of municipal wastewater treatment effluents,(179) of river water,(180) and of other water supplies.(181) Halogenated organic compounds were found by GC/MS/DS in water and in sediment samples taken from three tributaries of the Niagara River adjacent to hazardous waste disposal areas in Niagara Falls, New York.(182)

New mass spectrometric techniques have been applied to the analysis of organic constituents of aqueous media. Analyses of standard mixtures and some wastewater samples indicated the suitability of field desorption mass spectrometry for identification of organophosphorus pesticides at nanogram levels in the environmental samples without preliminary separation and purification.(183) The mass spectrometer has also been used as an element-specific detector for a gas chromatograph, where the GC effluent was atomized in a microwave-induced discharge located in the GC/MS/DS interface.(184) The elements investigated were fluorine, chlorine, bromine, iodine, sulfur, and nitrogen, but the method is applicable to other elements as well.

Summary

The application of GC/MS/DS methods to environmental analysis, especially the analysis of aqueous media, can easily be seen to be a rapidly expanding area. The use of the technique has become so common that only a few of the more unusual applications are reported in the literature, in spite of the fact that this type of analysis is being carried on in laboratories around the world. As rapidly as new GC or MS techniques are developed, they are applied to the analysis of organic constituents in aqueous media, either in the environmental or biomedical areas. The rapid growth of the field underscores the necessity for adherence to strict quality control measures, since the analyses are being performed at all levels of personnel experience and judgment. Standardized protocols which will allow interlaboratory comparison of data take on an increasingly important role. Many of the required quality control criteria and procedures are still in the process of development, and this area of quality control is probably the most important and rapidly developing area of research in the environmental field at present.

REFERENCES

1. a) Alford, A., Biomed. Mass Spectrom., 5, 259 (1978).
   b) Alford, A., Biomed. Mass Spectrom., 4, 1 (1977).
   c) Alford, A., Biomed. Mass Spectrom., 2, 229 (1975).
2. For a general review of mass spectrometry and instrumentation see, *e.g.*:
   a) Specialist Periodical Reports - Mass Spectrometry, Vol. 1-4, The Chemical Society, London.
   b) MTP International Review of Science, Physical Chemistry, Series I, Vol. 5, ed. Maccoll, A., Butterworth and Co. Ltd., Oxford, 1972 and more recent reports.
   c) Watson, J. T., Introduction to Mass Spectrometry, Raven Press, New York, 1976, 237 pp.

d) McFadden, W., Techniques of Combined Gas Chromatography: Mass Spectrometry, Wiley, New York, 1973.

3. Personal Communication (See Appendix A).
4. Manufacturers' advertising literature.
5. Waller, G. R., Biochemical Applications of Mass Spectrometry, Wiley Interscience, New York, 1972, 872 pp.
6. Beynon, J. H., Pure Appl. Chem., 50, 65 (1978).
7. Williams, D. H., I. Howe, Principles of Organic Mass Spectrometry, McGraw-Hill, Maidenhead, 1972, p. 177.
8. Hunt, D. F., Adv. Mass Spectrom., 6, 517, 1974 and references therein.
9. Millard, B. J., Quantitative Mass Spectrometry, Heyden & Son, London, 1978.
10. Dougherty, R. C., J. D. Roberts, F. J. Biros, Anal. Chem., 47, 54 (1975).
11. Dougherty, R. C., K. Piotrowska, Proc. National Acad. Sci. USA, 73, 777 (1976).
12. Dougherty, R. C., J. Dalton, F. J. Biros, Org. Mass Spectrom., 6, 1171 (1972).
13. Dougherty, R. C., K. Piotrowska, J. Assoc. Off. Anal. Chem., 59, 1023 (1976).
14. Horning, E. C., M. G. Horning, D. I. Carroll, I. Dzidic, R. N. Stillwell, Anal. Chem., 45, 936 (1973).
15. Dzidic, I., D. I. Carroll, R. N. Stillwell, E. C. Horning, Anal. Chem., 47, 1308 (1975).
16. Hunt, D. I., C. N. McEwen, T. M. Harvey, Anal. Chem., 47, 1308 (1975).
17. Busch, K. L., M. M. Bursey, J. R. Hass, Appl. Spectry., in press.
18. Hass, J. R., M. D. Friesen, D. J. Harvan, C. E. Parker, Anal. Chem., submitted.
19. Burlingame, A. L., Ecotox. and Environ. Safety, 1, 111 (1977).
20. Carlson, R. M., R. Cople, A. R. Dyler, K. J. Welch, D. L. Bodenner, R. Leukkonen, Environmental Impact and Health Effects. Vol. 2, R. L. Jolley, H. Gorchev and D. H. Hamilton, eds., Ann Arbor Science, 1975.
21. Dowty, B. J., D. R. Carlisle, J. L. Laseter, Environ. Sci. Technol., 9, 762 (1976).
22. Buelow, R., J. K. Carswell, J. M. Symons. J. Amer. Water Works Ass., 65, 57 (1973).

23. Glaze, W., J. Henderson, IV, G. Smith, Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, 1976.

24. McKinney, J. D., R. R. Mauser, J. R. Hass, R. O. Thomas, Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, 1976, p. 417.

25. Suffet, I. H., L. Brenner, J. T. Coyle, P. R. Cairo. Environ. Sci. Technol., 12, 1315 (1978).

26. Drevenkar, R. M., W. Giger, J. Chromatogr., 116, 43 (1976).

27. Masatoshi, M., N. Hiroshi, M. Shuichi, Tokyo Toritsu Eiseri Kenyusho Kenkyu Mempo, 25, 393 (1974).

28. Joe, F. J., Jr., D. A. Flene, C. M. Melltta, J. A. G. Roach, E. Rosboro, F. Fazeo, J. Assoc. Off. Anal. Chem., 60, 509 (1977).

29. Keith, L. H., W. Garrison, F. R. Allen, M. H. Carter, T. L. Floyd, J. D. Pope, A. D. Thruston, Jr.., Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, 1976, ch. 22.

30. Kopfler, F. C., R. G. Melton, R. D. Lingg, W. E. Coleman, Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, 1976, ch. 6.

31. Zlatkis, A., W. Bertsch, H. A. Lichtenstein, A. Tishbee, F. Shunbo, H. M. Lieluch, A. M. Coscia N. Fleischer, Anal. Chem., 45, 763 (1973).

32. Neely, M. A., R. Greenspun, R. A. Carr. Presented at ACS Meeting, Miami Beach, Division of Environmental Chemistry, September, 1978.

33. Ellgehausen, D., Anal. Lett., 8, 11 (1975).

34. Junk, G. A., J. J. Richard, M. D. Grieser, D. Witiak, M. D. Arguello, R. Veik, H. J. Svec, J. S. Fritz, G. V. Calder, J. Chromatogr., 99, 745 (1974).

35. Giger, W., M. Reinhard, C. Schaffne, Vom Wasser, 43, 343 (1974).

36. Smillie, R. D., A. A. Nicholson, O. Meresz, W. R. Duholke, G. A. V. Rees, K. Roberts, C. Fung, Organics in Ontario Drinking Waters. Part III. A Survey of Selected Water Treatment Plants, Ontario Ministry of the Environment, OTC 7703, Project No. AAN-7504, April, 1977.

37. Reinhart, D., J. Giger, J. Chromatogr., 116, 43 (1976).

38. Comstock, T., M. H. Makle, R. Matalox, Anal. Chem., 49, 386 (1977).

39. Jeone, I. J., G. A. Runeccius, E. L. Thomas, J. Food Chem., 24, 433 (1975).

40. Bertsch, W., E. Anderson, J. Chromatogr., 112, 701 (1975).

41. Bellar, T. A., J. J. Lichtenberg, J. W. Eichelberger, Environ. Sci. Technol., 10, 926 (1976).

42. Grob, K., J. Chromatogr., 84, 255 (1975).

43. Sievers, R. E., R. H. Shapiro, H. F. Walton, G. Ziceman, R. Barkley, "High Resolution Gas Chromatography", ed., S. P. Cram, Academic Press, New York, 1978.

44. Rook, J. J., A. P. Meijers, A. A. Grae, A. Noordaii, Vom Wasser, 44, 23 (1975).

45. Dowty, B., D. Carlisle, J. L. Laseter, Environ. Sci. Technol., 9, 762 (1975).

46. Dowty, B., D. Carlisle, J. L. Laseter, Science, 187, 75, 1975.

47. Deinzer, M., R. Melton, D. Mitchell, Water Res., 9, 799 (1975).

48. Coleman, W. E., R. D. Lingg, R. M. Melton, F. C. Kopfler, Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, 1976, ch. 21.

49. Tuessel, A., M. D. Umphres, L. Y. C. Leong, R. R. Tuessel, Water Chlorination. Environmental Impact and Health Effects. Vol. 2, R. L. Jolley, H. Gorchev and D. H. Hamilton, eds., Ann Arbor Science, 1975.

50. Sundstrom, G., O. Hutzinger, F. W. Karasek, J. Michnowicz, J. Assoc. Off. Anal. Chem., 59, 962 (1976).

51. Kubelka, V., J. Mitera, V. Rabl, J. Mostecky, Water. Res., 10, 137 (1976).

52. Fine, D. H., D. R. Rounbehler, N. P. Sen, J. Agr. Food Chem., 24, 980 (1976).

53. Smillie, R. D., T. Sakuma, W. K. Duholke, J. Environ. Sci. Health, A13, 187 (1978).

54. Pellizzari, E. D., N. P. Castillo, S. Willis, D. Smith, J. Bursey, Fuel Chemistry, in press.

55. Novak, J., J. Zlatecky, V. Kubelka, J. Mostecky, J. Chromatogr., 76, 45 (1973).

56. Zlatkis, A., W. Bertsch, D. A. Bafus, H. M. Liebich, J. Chromatogr., 91, 379 (1974).

57. Sickels, T. W., D. T. Stafford, Amer. Lab., p. 17, May, 1977.

58. Mattsson, P. E., Å. Norström, C. Rappe, J. Chromatogr., 101, 209 (1975).
59. Chau, A. S., J. A. Coburn, J. Assoc. Off. Anal. Chem., 57, 389 (1974).
60. Bean, R. M., R. G. Riley, P. W. Ryan, in Water Chlorination. Environmental Impact and Health Effects, L. H., ed., Ann Arbor Sciences, 1975, Ch. 17.
61. Harris, L. E., W. L. Buckle, J. W. Eichelberger, Anal. Chem., 46, 1912 (1974).
62. Bertsch, W., E. Anderson, J. Chromatogr., 126, 213 (1976).
63. Cautreels, W., K., Van Cauwenberghe, Atom. Environ., 10, 447 (1976).
64. Meinema, H. A., T. Burger-Wiersma, G. Versluis-deHaan, E. Ch. Gevers, Environ. Sci. Technol., 12, 288 (1978).
65. John, E. D., G. Nickles, J. Chromatogr., 138, 399 (1977).
66. Mory, W. C., S. N. Chester, J. Pleam, B. H. Glump, H. S. Hertz, D. P. Engonian, S. M. Dyaszel, J. Chromatogr. Sci., 13, 535 (1975).
67. Lingg, R. D., R. G. Melton, F. C. Kopfler, W. E. Coleman, D. E. Mitchell, J. Assoc. Off. Anal. Chem., 69, 605 (1977).
68. Dunlap, W. J., D. C. Shew, M. R. Scalf, R. L. Cosby, J. M. Robertson. Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, 1976, ch. 27.
69. Novotny, M., M. L. McConnell, M. L. Lee, R. Farlow, Clin. Chem., 20, 1105 (1974).
70. Brown, R. A., H. L. Huffman, Science, 191, 847 (1976).
71. Pellizzari, E. D., N. P. Castillo, S. Willis, D. Smith, J. T. Bursey, ASTM, in press.
72. Maseurs, M., J. Spignette, H. Miller, EPA Contract No. 68-03-2343, Midwest Research Institute.
73. Lichtenberg, J. J., IEEE Transactions on Nuclear Science, Vol. NS-22, No. 2, April, 1975.
74. Ewing, B. B., E. S. K. Chian, J. C. Cook, C. A. Evans, P. K. Kopke, E. G. Perkins, Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters, Final report. EPA-560/6-77-015 (1977).
75. Mieure, J. P., M. W. Dietrich, J. Chromatogr. Sci., 11, 559 (1973).
76. Chian, E. S. K., P. P. K. Kuo, W. J. Cooper, W. F. Cowen, R. C. Fuentes, Environ. Sci. Technol., 11, 282 (1977).
77. Pitt, W. W., Jr., R. L. Jolley, S. Katz, Identification and Analysis of

Organic Pollutants in Water, L. H. Keith, ed. Ann Arbor Science, 1976, ch. 14.

78. Burnham, A. K., G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec, R. Willis, Anal. Chem., 44, 139 (1972).

79. Karasek, F. W., Ind. Res. Devel., 113 (1978).

80. Coburn, J. A., A. S. Y. Chau, J. Assoc. Off. Anal. Chem., 59, 862 (1976).

81. Lindstrom, K., J. Nordin, J. Chromatogr., 128, 13, (1976).

82. Lawrence, K. H., Environ. Sci. Technol., 10, 555 (1976).

83. Kuehl, D. W., G. D. Veith, E. M. Leonard, Water Chlorination. Environmental Impact and Health Effects. Vol. 2, R. L. Jolley, H. Gorchev and D. H. Hamilton, eds., Ann Arborn Science, 1975.

84. Registry of Mass Spectral Data. Vols. 1-4, Stenhagen, E., S. Abrahamsson, F. W. McLafferty, Eds., John Wiley and Sons, New York, New York, 1974.

85. Eight Peak Index of Mass Spectra, Vol. I and III, Mass Spectrometry Data Centre. AWRE, Aldermaston, Reading, RG74PR, UK, 1974.

86. Compilation of Mass Spectral Data, Cornu, A., R. Massot, eds., and Son, Ltd., London, 1966.

87. Brenner, L., B. Silver, I. Suffet, J. Environ. Sci. Health, A13 (2), 149 (1978).

88. U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants. Cincinnati, Ohio, 1977.

89. Merritt, C., Jr., P. Issenberg, M. L. Bazinek, D. N. Green, T. O. Merren, J. G. Murray, Anal. Chem., 37, 1037 (1965).

90. McMurray, W. J., B. N. Greene, S. R. Lipsky, Anal. Chem., 38, 1194 (1966).

91. Burlingame, A. L., D. H. Smith, R. W. Olsen, Anal. Chem., 40, 13 (1968).

92. Hites, R. A., K. Biemann, Anal. Chem., 40, 1217 (1968).

93. Watson, J. T., D. R. Pelster, B. J. Sweetman, J. C. Frolich, J. Oats, Anal. Chem., 45, 2071 (1973).

94. Leibrand, R., D. Jackson, Proceedings of 25th Annual Conference on Mass Spectrometry and Allied Topics, June 1977, p. 269.

95. Schnute, W. C., Jr., Proceedings of 25th Annual Conference on Mass Spectrometry and Allied Topics, June 1977, p. 650.

96. Hites, R. A., K. Biemann, Anal. Chem., 42, 855,(1970).

97. Biller, J. E., K. Biemann, Anal. Lett., 7, 515 (1974).

98. Dromey, R. G., M. J. Stetik, T. C. Rindfleisch, A. M. Duffield, Anal. Chem., 48, 1368 (1976).

99. Buchanan, B. G., D. H. Smith, W. C. White, R. J. Gritten, E. A. Feigenbaum, J. Lederberg, C. Djerassi, J. Am. Chem. Soc., 98, 6168 (1976).

100. Jurs, P. C., B. R. Kowalski, T. L. Isenhour, Anal. Chem., 41, 21(1969).

101. Dayringer, H. E., F. W. McLafferty, Org. Mass Spectrom., 11, 543 (1976) and earlier papers in this series.

102. Hertz, H. S., R. A. Hites, K. Biemann, Anal. Chem., 43, 681 (1971).

103. Milne, G. W. A., S. R. Heller, in Computer Assisted Structure Elucidation, Smith, D. H. ed., ACS Symposium Series #54, American Chemical Society, Washington, 1977, p. 26.

104. Pesyna, G. M., R. Venkataraghavan, H. E. Dayringer, F. W. McLafferty, Anal. Chem., 48, 1362 (1976).

105. Heller, S. H., "Methods and Standards for Environmental Measurement. Kirchhoff, W. H., ed., N. B. S. Publication #464, National Bureau of Standards, Gaithersburg, MD, p. 75.

106. Mitra, G. D., G. Mohan, A. Sinha, J. Chromatogr., 99, 215 (1974).

107. Smith, D. H., M. Achenback, W. J. Yeager, P. J. Anderson, W. L. Fitch, T. C. Rindfleisch, Anal. Chem., 49, 1962 (1977).

108. Gates, S. C., M. J. Smisko, C. L. Ashendel, N. D. Young, J. F. Holland, Anal. Chem., 50, 433 (1978).

109. Budde, W. L., J. W. Eichelberger, J. Chromatogr., 134, 147 (1977).

110. Wood, K. V., R. H. Grange, J. W. Taylor, Anal. Chem., 50, 1652 (1978).

111. De Ridder, J. J., P. C. J. M. Koppens, H. J. M. Van Hall, J. Chromatogr., 143, 281 (1977).

112. Miller, W., J. S. Wilkins, L. L. Dunham, J. Assoc. Off. Anal. Chem., 58, 10 (1975).

113. Shinohara, R., M. Kogan, J. Shinohara, T. Hori, Chem. Abstracts 88: 110286x,
Kitakyushu Munic. Inst. Environ. Health Sci., 26, 856 (1977).

114. Blaser, W. W., R. A. Bredeweg, L. A. Shadoff, R. H. Stehl, Anal. Chem., 48, 984 (1976).

115. Shadoff, L. A., R. A. Hummel, L. Lamparski, Bull. Environ. Contam. Toxicol., 18, 478 (1977).

116. Fujii, T., J. Chromatogr., 139, 297 (1977).

117. Fujii, T., Anal. Chem., 49 1985 (1977).

118. Sen, W.P., W. F. Miles, S. Seciman, J. T. Lawrence, J. Chromatogr., 128, 161 (1976).

119. Sumino, K., Arch. Environ. Contam. Toxicol., 6, 365 (1977).

120. Fujii, T., Bull. Chem. Soc. Japan, 50, 2911 (1977).

121. Budde, W. L., J. W. Eichelberger, J. Chromatogr., 134, 147 (1977).

122. Richard, J. J., G. A. Junk, M. D. Avery, M. L. Nehring, J. Frite, H. J. Svec, Pest. Mon. J., 9, 117 (1975).

123. Kuehl, D. W., Anal. Chem., 49, 521 (1977).

124. Eichelberger, J. W., L. E. Harris, W. L. Budde, Anal. Chem., 46, 227 (1974).

125. Perry, P. L., C. J. Chen, G. A. Jungclaus, P. S. Warner, Identification of Organic Compounds in Industrial Effluent Discharges, Battelle.

126. Bursey, J. T., D. Smith, J. E. Bunch, R. N. Williams, R. E. Berkley, E. D. Pellizzari, Am. Lab., 9, 35 (1977).

127. Environmental Protection Agency - Office of Enforcement. National Field Investigations Center - Denver - Laboratory Manual.

128. e.g., Jungclaus, G. A., D. S. Warner, C. C. Chuang, Final Report on Analysis of Municipal Wastewaters for Priority Pollutants to Municipality of Metropolitan Seattle, Battelle Columbus Laboratories (1978).

129. Beggs, D., Am. Lab., 10, 81 (1978).

130. Damico, J. N., R. P. Barron, Anal. Chem., 43, 117 (1971).

131. Games, D. E., A. H. Jackson, D. S. Millington, M. Rossiter, Biomed. Mass Spectrom., 1, 5 (1974).

132. Eichelberger, J. W., L. E. Harris, W. L. Budde, Anal. Chem., 47, 995 (1975).

133. American Society for Testing and Materials Committee D-21, 21st Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, California, May 20-25, 1973.

134. Middleditch, B. S., Anal. Chem., 41, 2092 (1969).

135. Wallick, R. H., G. L. Peele, [illegible] B. Hynes, Anal. Chem., 41, 388 (1969).

136. Schoengold, D. M., W. H. Stewart, Anal. Chem., 44, 884 (1972).

137. Bellar, T. A., W. L. Budde, J. w. Eichelberger, Am. Chem. Soc. Symp. Ser., 94, 49 (1979).

138. Bishop, D. F., U. S. Environ. Prot. Agency, Off. Res. Dev. (Report), EPA-600/S2-80-196 (1980), 5 pp.

139. Knoeppel, H., Ann. Chim., 67, 649 (1977).

140. Hites, R. A., Adv. Chromatogr. (N.Y.), 14, 69 (1977).

141. Meek, D., Water Res. Top., 1, 164 (1981).

142. McGuire, J. M., R. G. Webb, Pollut, Eng. Technol., 18, 1 (1981).

143. Keith, L. H., J. Chromatogr. Sci., 17, 48 (1979).

144. Cornu, A., J. C. Leclerc, R. Massot, Bull. Inf. Sci. Tech., Commis. Energ. At. (Fr.), 230-231, 181-3 (1979).

145. Carson, B. L., J. E. Going, V. Lopez-Avila, J. L. McCann, C. J. Cole, J. L. Holt, in Advances in the Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, 1981, Vol. 2, Ch. 32.

146. Shackelford, W. M., L. H. Keith, in "Frequency of Organic Compounds Identified in Water," U.S. EPA Report, EPA-600/4-76-062, PB-265470, National Technical Information Service, Springfield, VA (1976).

147. Beggs, D., Environ. Sci. Res., 16, 303 (1978, Pub. 1980).

148. Beggs, D. P., Am. Lab., 10, 81 (1978).

149. Beggs, D., NBS Spec. Publ. (U.S.), 519, 169 (1979).

150. Beggs, D. P., Oesterr. Chem. Z., 81, 98 (1980).

151. Beggs, D. P. Pergamon Ser. Environ. Sci., 3, 317 (1980).

152. Shackelford, W. M., D. M. Cline, L. Burchfield, L. Faas, G. Kurth, A. D. Sauter, in Advances in the Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, 1981, Vol. 2, Ch. 33.

153. Dromey, R. G., J. Stefik, T. C. Rindfleisch, A. M. Duffield, Anal. Chem., 48, 1368 (1976).

154. Pesyna, G. M., R. Venkataraghavan, H. E. Dayringer, F. W. McLafferty, Anal. Chem., 48, 1362 (1976).

155. Rosenthal, D., Anal. Chem., 54, 63 (1982).

156. Coleman, W. E., W. K. Allen, R. W. Slater, S. J. Voto, R. G. Melton, F. C. Kopfler, T. A. Aurand, Presented at the Second Chemical Congress of the North American Continent, Las Vegas, NV, August 24-29 (1980).

157. Sauter, D., C. Kieda, R. Devine, H. Nowicki, ASTM Spec. Tech. Publ. STP686, 221 1978 (Pub. 1979).

158. Sauter, A. D., L. D. Betowski, T. R. Smith, V. A. Strickler, R. G. Beimer, B. N. Colby, J. E. Wilkinson, J. High Resolut. Chromatogr. Chromatogr. Commun., 4, 366 (1981).

159. Budde, W. L., J. W. Eichelberger, An EPA Manual for Organics Analysis Using Gas Chromatography - Mass Spectrometry, EPA/600/8-79/006 (1979); Order No. PB-297164, 166 pp.

160. Matsunaga, K., F. Shibata, N. Saito, N. Torigashi, K. Kenmochi, Y. Ogino, Okayama-ken Kankyo Hoken Seuta Nempo, 3, 192 (1979).

161. Ingram, L. L., Jr., G. D. McGinnis, S. V. Parikh, Anal. Chem., 51, 1077 (1979).

162. Frame, G. M., Control Hazard. Mater. Spills, Proc. Natl. Conf., 180 (1980).

163. Maier, E. J., G. Fritschi, H. Kussmaul, Vom Wasser, 51, 227 (1978).

164. Baehn, U., B. Bohn, G. Fritschi, E. Maier, M. Sonnenborn, Hydrochem. Hydrogeol. Mitt., 3, 75 (1978).

165. Shinohara, R., M. Koga, A. Kido, S. Eto, T. Hori, T. Akiyama, Koenshu-Yro Masu Kenkyukai, 3, 69 (1978).

166. Koga, M., R. Shinohara, A. Kido, S. Eto, Koenshu-Iyo Masu Kenkyukai, 4, 153 (1979).

167. Brookes, B. I., S. M. Jickells, R. S. Nicolson, J. Assoc. Public Anal., 16, 117 (1978).

168. Lin, D. C. K., R. L. Foltz, S. V. Lucas, B. A. Petersen, L. E. Slivon, R. G. Melton, ASTM Spec. Tech. Publ., STP686, 68 (1978; Pub. 1979).

169. Shinohara, R., A. Kido, S. Eto, T. Hori, Kankyo Osen Busshitsu to Sono Tokishikorojii Shinpojumu [Koen Yoshishu], 6th, 34 (1979).

170. Pereira, W. E., B. A. Hughes, J. Am. Water Works Assoc., 72, 220 (1980).

171. Suffet, I. H., L. Brenner, P. R. Cairo, Water Res., 14, 53 (1980).

172. Hartmetz, G., J. Slemrova, Bull. Environ. Contam. Toxicol., 25, 106 (1980).

173. Hites, R. A., Pergamon Ser. Environ. Sci., 3 281 (1980).

174. Lopez-Avila, V., R. A. Hites, Pergamon Ser. Environ. Sci., 3, 293 (1980).

175. Oldham, R. G., R. L. Spraggins, K. W. Lee, L. H. Keith, Prepr. Pap. Natl. Meet. - Am. Chem. Soc., Div. Environ. Chem., 18, 626 (1978).

176. James, H. A., M. Fielding, T. M. Gibson, C. P. Steel, Adv. Mass Spectrom., 8B, 1429 (1980).

177. Shinohara, R., M. Koga, A. Kido, S. Eto, T. Tabata, T. Hori, T. Akiyama, Environ. Int., 4, 163 (1980).

178. Shinohara, R., A. Kido, S. Eto, T. Hori, M. Koga, T. Akiyama, Water Res., 15, 535 (1981).

179. Bishop, D. F., GC/MS Methodology for Priority Organics in Municipal Wastewater Treatment, EPA-600/2-80-196 (1980); Order No. PB81-127813 (NTIS), 52 pp.

180. Yasuhara, A., H. Shiraishi, M. Tsuji, T. Okuno, Environ. Sci. Technol., 15, 570 (1981).

181. Dmitriev, M. T., E. G. Rastyannikov, S. A. Volkov, Vodosnabzh. Sanit. Tech., 4, 5 (1981).

182. Elder, V. A. B. L. Proctor, R. A. Hites, Biomed. Mass Spectrom., 8, 409 (1981).

183. Schulten, H. R., S. E. Sun, Int. J. Environ. Anal. Chem., 10, 247 (1981).

184. Treudenthal, J., Int. J. Environ. Anal. Chem., 5, 311 (1978).

SECTION 9

QUALITY ASSURANCE/QUALITY CONTROL

DEFINITION OF TERMS

There appear to be different interpretations of the various terms used to maintain and quantify the satisfactory implementation of a particular analytical method. For the sake of clarity, those terms most frequently used will be discussed.

Quality Assurance

Quality assurance is a system of independent checks or a supervision of each phase of the analysis - from the preparation of material through sample collection, work-up, analysis and data interpretation and reporting. Its function is to "assure" that sampling and analytical protocols are executed in such a way as to insure the integrity of the data.

Quality Control

Quality control is concerned with the assignment of a numerical value to the result of the analysis scheme, primarily, but not exclusively by analysis of blanks and controls. Two additional major contributions to quality control are method validation and recovery studies, both being concerned with identification and quantitation of sources of error.

Accuracy and Precision

The closeness of the experimentally determined value to the true value is defined as the accuracy while the reproducibility or agreement between values obtained by replicate analyses of the same sample is defined as precision. Accuracy and precision are a reflection of error, both determinate and indeterminate, associated with the analysis. Personal, instrumental and methodological errors are considered determinate while indeterminate errors are random and arise from the degree of uncertainty inherent in any physical measurement. Commonly, error is quantified in terms of standard deviation and variance.(1)

QUALITY ASSURANCE

The maintenance of sample integrity should be continuous and inherent in both the sampling and analytical protocols. Paramount to this is accurate record keeping and labeling in all phases of sample handling.(2) It is essential that the condition and location of the sample be carefully documented so that subsequent suspicions of sample quality may be substantiated or refuted.

Preparation of Materials

Preparation of materials and equipment for sample collection should be carried out with an awareness for subsequent analytical procedures. Glassware should be detergent washed, distilled water and solvent rinsed and finally heated at 450°C for several hours to remove all residual organics.(3,4) Other materials, such as sample collection devices should be solvent or distilled water rinsed and air-dried. The requisite purity of solvents, reagents, gases, standards and distilled water must be attained and/or verified according to their intended use. Solvents, used for extraction may contain impurities which would be amplified by as much as several orders of magnitude during extract concentration and should therefore be freshly redistilled and stored in inert containers in the dark. Chemical reagents, particularly sodium sulfate used for dehydrating solvent extracts and packing materials used for open-column chromatographic clean-up operations, should be solvent extracted and heated to 300°C prior to use.(4) Other reagents, such as materials added to the sample as preservatives should be scrutinized for purity and redistilled or recrystallized as necessary.

Sorbent materials (*e.g.*, XAD, Tenax GC, Chromosorb 101, activated carbon) used as collection media for purge and trap must be exhaustively extracted and thermally desorbed in an inert gas stream prior to use.(5) Background levels of these sorbent materials should be verified by gas chromatographic analysis before deployment to the field.

Purge and trap analysis for volatile materials in water requires that substantial quantities of helium or nitrogen be passed through the sorbent cartridge. This presents a significant potential for contamination, particularly by hydrogen impurities in cylinder gases. In addition, appreciable quantities of oxygen commonly found in such gases might cause chemical alterations in certain organic species. Oxygen can be removed by any one of a number of commercially available oxygen scrubbing traps. Organic impurities in reagent gases can be readily removed by cryogenic trapping using liquid nitrogen or by adsorption on an activated carbon column.(6) Purge gas (volatile organic analysis) purity can be verified by performing the purge analysis in the absence of a sample and analyzing the exposed sorbent trap by gas chromatography. Gases employed specifically for gas chromatography (e.g., carrier and flame gas) should be similarly cleaned.

The overall accuracy of the analysis is a function of many factors, one of the most important being the purity of the standard(s) used for quantitation. Standard purity is crucial to accurate results. In most cases, reliance on purity reported by the commercial supplier is unsatisfactory and verification must be made by the analyst. Standard solutions should be analyzed by the technique to be used for sample analysis. Impure standards may be purified by a variety of techniques including distillation, recrystallization, column chromatography and solvent fractionation.

Distilled water, used primarily for the preparation of blanks and controls, must be free of the types of compounds to be determined in the field collection of water samples. Very different water purification mechanisms need to be invoked depending upon these two basic conditions. Generally as a minimum treatment, tap water should be filtered, distilled, deionized (or vice versa), passed through activated carbon and, if necessary, stored under ultraviolet light. Further, reagent water should be extracted, purged, etc. via the analytical protocol to be employed for the actual samples to remove additional contaminants which would interfere with a particular analysis.(6)

Sample Collection

Collection of a water sample which is truly representative of the matrix at large is not a trivial matter. No single collection technique can be proposed to achieve this end for every analysis, water type, or compounds of interest. This is especially important with respect to volatile compounds. Such materials can only be collected by grab techniques since intermitent or composite sampling involves a pumping device which would undoubtedly result in appreciable losses of volatile species. A Teflon boiling device has been designed for sampling ground water to be analyzed for volatiles.(7) Less stringent sample collection requirements need be imposed where semi and nonvolatile compounds are concerned. In these cases, integrated sampling may achieve a more representative sample.(3)

Storage and Analysis

Water samples are generally stored in Teflon®-lined, amber glass,(8) screw cap bottles at 4°C(9) while awaiting analysis. Preservation with materials such as ascorbic acid(10) or potassium ferricyanide(11) have been done although little is known about the overall effects of adding these compounds. Adjustment of pH prior to storage of pesticide-containing samples was found to be crucial.(9) Alternatively, extraction of components may be carried out at the collection site.* This has been done most frequently with adsorption columns for semi and nonvolatiles although studies have also shown a field device to be quite effective for isolating volatiles(12) by purge and trap. In this way the sample can be stored isolated from its matrix and therefore any modification (*e.g.*, adsorption, precipitation, volatilization) which may have occurred therein during storage. Optimum analysis times must be determined for each sample type and analysis scheme.

Ideally, the analysis of samples should be done sequentially with the analysis of blanks, both sample and reagent,(13,14) controls and standards. Special attention should be paid to memory effects from previous samples, particularly with automated devices which employ solenoid-activated valves and extensive transfer tubing.(6) Replicate analyses, both in terms of sample preparation and instrumental redetermination of the same sample, are important not only to improve the precision and accuracy of the analysis but also to invalidate spurious results.

Gas chromatographic analysis, if employed, should include frequent solvent and air injection blanks to identify sources of contamination from the solvent, column bleed, syringe and carrier gas.(2) In addition, careful detector calibration (*e.g.*, determination of linear dynamic range, optimizing flame conditions for FID) or applied voltage/pulse interval for ECD should be done on a regular basis (at least weekly) and the performance recorded in an instrument log book.(2)

Calibration is especially important for gas chromatography/mass spectrometry systems.(14) Quantitation mechanisms, whether automated (electronic peak integration) or manual (peak height measurement, planimetry) should be examined at least daily.

QUALITY CONTROL

Each step in the sampling and analysis protocols must be validated with representative compounds in authentic or closely-approximating synthetic sample matrices prior to the analysis of real samples.(15) Generally, the method is validated inclusively by a recovery study, wherein the sample is spiked with known compounds, carried through the analysis scheme and their percent recovery is determined. Alternatively, an internal standard, which can be easily recognized and is not present in the sample, can be added to the sample immediately after collection and the recovery of sample components assessed by the recovery of the standard.(14,16) Complimentarily, a study should be done on error propagation(3) by assignment of a degree of uncertainty to each experimental operation. An error assessment must be made of each step of the analysis from sample collection through data interpretation. The total error, S_T, associated with the reported concentrations may be estimated by

$$S_T = \left[\sum_{i=1}^{n} S_i^2 \right]^{1/2}$$

where S_i is the error associated with the i^{th} source of error.

Inherent in trace organic analysis, regardless of the level of quality assurance, is a certain degree of error. The sources of error are inumerable but include losses and contamination during sample collection, storage and analysis. The preparation of blank and control samples is intended to quantitate this error. Both blanks and controls should be prepared coincident with the preparation of the sample containers and should comprise at least 10 percent of the total number of samples collected.(2) Blanks and controls must accompany the samples during all phases of analysis. Control samples should be spiked with approximately the same level of compounds expected for the actual samples.

Blanks are intended to identify sample contamination, particularly but not exclusively during storage. In this regard, appreciable levels of Freons in samples have been traced to storage refrigerators and freezers.(6) Controls provide a measure of sample losses through, among other, incomplete isolate of sample components adsorption on glass surfaces and particulate material, decomposition and volatilization during storage and variations in instrument response. Reproducibility also provides information on validity through establishment of confidence limits on the result.

Interlaboratory calibration studies are extremely useful measures for assessing the degree of uncertainty of the result. It has been found that the agreement of several laboratories' analyses of a standard solution (containing various aromatics) by GC/ECD is excellent (<10% variation).(17) However, assessment of total error $\left(\frac{[\text{Mean error} + 2\ \text{S.D.}]100}{\text{True value}}\right)$ in the analysis of ten pesticides in twelve samples by XAD adsorption and solvent extraction revealed between 51 and 76% total error for a given compound and 48-160% for a given laboratory.(17) In another study, the variation in petroleum hydrocarbon content, determined by solvent extraction followed by column or thin-layer chromatography, among several laboratories was as high as 300%.(16) Such results suggest that a great deal of caution needs to be exercised during the interpretation of "trace level" results.(16) An extensive intra- and interlaboratory quality control discussion is given by Sherma.(18)

In conclusions, the quality of the analytical result is a function of each of the component steps of the analysis. The application of generous quality assurance and quality control procedures is intended to insure optimum validity of the data.

REFERENCES

1. Skoog, D. A., D. M. West, Fundamentals of Analytical Chemistry, Holt, Rinehart and Winston, 1966, pp. 33-57.
2. Fairless, B., Quality Assurance Practices and Procedures, U. S. Environmental Protection Agency, EPA-905/4-77-004, 297 pp., (1977).

3. Erickson, M. D., R. A. Zweidinger, L. C. Michael, E. D. Pellizzari, Environmental Monitoring Near Industrial Sites: Polychloronaphthalenes, U. S. Environmental Protection Agency, EPA-560/6-77-019, 266 pp., (1977).
4. Duinker, J. C., M. T. J. Hillebrand, J. Chromatogr., 150, 195 (1978).
5. Pellizzari, E. D., R. A. Zweidinger, M. D. Erickson, Environmental Monitoring Near Industrial Sites: Brominated Chemicals, Part II, U. S. Environmental Protection Agency, EPA-560/6-78-002, 165 pp., June (1978).
6. Lee, K. W., L. H. Keith, R. G. Oldham, L. P. Provost, P. H. Lin, G. L. Sellman, D. L. Lewis, An Evaluation of Purging Methods for Organics in Water, Prepared for: International Symposium on the Analysis of Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, Ontario, Canada, 1978, 21 pp.
7. Dunlap, W. J., J. F. McNabb, M. R. Scalf, R. L. Cosby, Sampling for Organic Chemicals and Microorganisms in the Subsurface, U. S. Environmental Protection Agency, EPA-600/2-77-176, 35 pp., August (1977).
8. Adams, J. W., T. E. Doerfler, C. H. Summers, Effect of Handling Procedures on Sample Quality, U. S. Environmental Protection Agency, EPA-600/7-78-017, 58 pp., (1978).
9. Millar, J. D., R. E. Thomas, D. E. Johnson, Development and Application of Test Procedures for Specific Toxic Substances in Wastewaters, Category 10: Pesticides and PCB's, Phase I Report, U. S. Environmental Protection Agency, Contract No. 68-03-2606, 112 pp., (1978).
10. Vogt, C. R., K. R. Leimer, Trace Subst. Environ. Health, 11, 358 (1977).
11. Kopfler, F. C., R. G. Melton, R. D. Lingg, W. E. Coleman, GC/MS Determination of Volatiles for the National Organics Reconnaissance Survey (NORS) of Drinking Water, in Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, Ann Arbor, MI, 1976, pp. 87-104.
12 Keith, L. H., K. W. Lee, L. P. Provost, D. L. Present, Methods for Gas Chromatographic Monitoring of EPA's Consent Decree Priority Pollutants, Prepared for: ASTM Symposium on Measurement of Organic Pollutants in Water, Denver, CO, 1978, 44 pp.

13. Eichelberger, J. W., W. M. Middleton, W. L. Budde, Analytical Quality Assurance for Trace Organic Analysis by Gas Chromatography/Mass Spectrometry, U. S. Environmental Protection Agency, EPA-600/4-75-007, 17 pp., (1975).

14. Lin, D. C. K., D. A. Contos, R. L. Foltz, V. R. Goff, T. L. Hayes, P. P. Kelly, S. V. Lucas, B. S. Mackey, B. A. Peterson, L. E. Slivon, R. Warren, S. C. Watson, GC/MS Analysis of Organics in Drinking Water Concentrates and Advanced Waste Treatment Concentrates, Vol. 1, U. S. Environmental Protection Agency, Contract 68-03-2548, 103 pp., (1978).

15. Lewis, R. G., Accuracy and Trace Organic Analyses, U. S. Environmental Protection Agency, EPA-600/J-76-076, 27 pp., (1976).

16. Hilpert, L. R., M. E. May, S. A. Wise, S. N. Chester, H. S. Hertz, Anal. Chem., 50(3), 458 (1978).

17. Aspila, K. I., J. M. Carron, A. S. Y. Chau, J. Ass. Offic. Anal. Chem., 60(5), 1097 (1977).

18. Sherma, J. Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples, U. S. Environmental Protection Agency, EPA-600/1-76-017, 287 pp. (1976).

APPENDIX A

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APPENDIX B

GC STATIONARY PHASES USED FOR ANALYSIS OF ORGANICS IN WATER

Table 1B. HALOGENATED ALIPHATIC COMPOUNDS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Aue*	✓				✓	✓			✓	90
Carbowax 400	✓				✓	✓		✓		(Appendix A)
Carbowax 1500	✓	✓	✓	✓	✓	✓	✓	✓		8,18,19,28,37,38,55,57,100,110,117 (Appendix A)
Carbowax 20M	✓	✓	✓	✓	✓	✓	✓	✓	✓	9,14,17,44,110,117,131,144,161
Chromosorb 101*	✓			✓	✓	✓	✓	✓		10,11,36,128,130 (Appendix A)
Chromosorb 102*	✓			✓		✓		✓		110
DC-200	✓				✓	✓		✓		60,87,153
Dexsil 300	✓			✓	✓	✓	✓	✓		49,83
Dexsil 410	✓				✓			✓		(Appendix A)
Diglycerol	✓				✓			✓		62,63
Emulphor ON 870	✓		✓		✓	✓		✓		12,64
FFAP	✓			✓	✓	✓	✓	✓		18,19,110,144,168
OV-1	✓	✓		✓	✓			✓	✓	17,30,49,54,86,89,144 (Appendix A)
OV-3	✓			✓	✓					140
OV-17	✓			✓	✓	✓	✓	✓		17,49,51,56,57,96,97,119,127,128 (Appendix A)
OV-17/QF-1	✓	✓		✓	✓	✓	✓	✓	✓	26,49,51,60,87,128,153
OV-17/QF-7	✓				✓					125
OV-17/OV-210	✓			✓					✓	17,103
OV-61			✓		✓	✓	✓	✓		68
OV-101	✓	✓	✓	✓	✓	✓	✓	✓		7,14,17,31,49,68,84,117,115 (Appendix A)
OV-101/Reoplex	✓								✓	103
OV-101 + UCON HB			✓			✓	✓	✓		65
OV-210	✓			✓				✓		17,49,87
OV-225	✓								✓	103
Porapak Q*	✓				✓					139,155 (Appendix A)
Reoplex										50

(Continued)

Table 1B (cont'd)

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
SE-30	✓	✓	✓		✓	✓	✓	✓	✓	10,17,18,39,49,62,63,103,110,160, 162,166, (Appendix A)
SE-30/OV-210	✓							✓	✓	103,169
GE SE-96 Igepal CO 880		✓	✓					✓	✓	44,45 (Appendix A)
SF-96			✓		✓	✓	✓	✓		68,95, (Appendix A)
SP-1000	✓		✓					✓		35,106
SP-2100	✓		✓		✓	✓		✓	✓	17,35,54,92,106, (Appendix A)
SP-2250/2401	✓						✓			46
Tenax GC*	✓			✓	✓	✓	✓	✓		17,19,36,108,129
UCW-98	✓				✓			✓		153

Table 2B. HALOGENATED AROMATIC COMPOUNDS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 400	✓				✓			✓		Appendix A
Carbowax 1500	✓			✓	✓	✓	✓	✓		19,28,55,57,110(Appendix A)
Carbowax 20M	✓	✓	✓	✓	✓	✓	✓	✓	✓	14,110,117,131,137,137,138 144,161
Chromosorb 101*	✓			✓	✓	✓	✓	✓		10,36,128,130
Chromosorb 102*	✓				✓	✓		✓		110
DC-200	✓				✓			✓		60,87,143,153
Dexsil 410	✓				✓			✓		(Appendix A)
Emulphor ON 870			✓		✓	✓		✓		12,64
FFAP	✓			✓	✓	✓	✓	✓		19,110,144
OV-1	✓	✓	✓	✓	✓			✓		17,30,86,89,122,143,144 (Appendix A)
OV-1,QF-1										
OV-17/XE60	✓			✓				✓		3
OV-3	✓				✓			✓		140,148 (Appendix A)
OV-17	✓				✓	✓	✓	✓	✓	17,50,56,73,96,97,127,128, 162, (Appendix A)
OV-17/OV-210	✓			✓	✓	✓	✓	✓		104
OV-17/QF-1	✓	✓		✓		✓	✓	✓		3,20,23,25,26,48,51,60,57,122, 125,153
OV-61			✓		✓	✓	✓	✓		67
OV-101	✓	✓	✓	✓	✓	✓	✓	✓	✓	17,31,68,99,119,136,137,135 148,151 (Appendix A)
OV-101/OV-210	✓					✓	✓	✓		23
OV-101/QF(1&3)	✓			✓						95
OV-101/UCON HB			✓			✓	✓	✓		65
OV-210	✓				✓	✓		✓		87,162 (Appendix A)
OV-225	✓					✓	✓	✓		23
QF-1	✓							✓	✓	143
Reoplex	✓				✓					50
SE-30	✓	✓	✓	✓	✓	✓	✓	✓	✓	10,17,39,96,107,110,160,161 (Appendix A)

(continued)

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Table 2B (cont'd)

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
SE-30/OV-210	✓			✓	✓	✓	✓	✓		104,122
SE-54			✓	✓				✓		(Appendix A)
SF-96			✓		✓	✓	✓	✓		68,95 (Appendix A)
SP-1000	✓		✓		✓			✓		35,106
SP-2100	✓		✓					✓	✓	35,92,106,141
SP-2250/2401		✓					✓			109
Tenax GC*	✓			✓	✓	✓	✓	✓		19,36
UCON HB 5100			✓	✓						67
UCON LB 550			✓	✓						67
UCW-98	✓				✓					153
DERIVATIZED HALOGENATED AROMATIC COMPOUNDS:										
FFAP	✓			✓						74
OV-17/QF-1	✓		✓				✓	✓		2,80
SP-2401	✓			✓						101
OV-101/OV 210	✓							✓		2
OV-225	✓							✓		2
SP-2250/2401	✓							✓		2
SE-30			✓					✓	✓	107

Table 3B. DERIVATIZED AMINO ACIDS

ATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
V-1	✓							✓		24
V-7/OV-22	✓								N.G.	64
V-101	✓			✓						152
P-2100	✓								✓	141

Table 4B. PHOSPHORUS COMPOUNDS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 20M	✓		✓		✓	✓	✓	✓	✓	47,93,112,131,161
Dexsil 300	✓							✓	✓	22,49
Dexsil 400	✓			✓	✓					120
DC-200	✓							✓	✓	22,60
OV-1	✓	✓		✓	✓			✓	✓	17,30,47,49,86,112,143, (Appendix A)
OV-3	✓			✓				✓		148
OV-17	✓				✓	✓		✓		17,28,50,149,97 (Appendix A)
OV-17/OV-210	✓								✓	103
OV-17/QF-1	✓	✓		✓	✓	✓	✓	✓	✓	26,49,51
OV-101	✓		✓	✓	✓	✓	✓	✓		17,31,49,60,87,117
OV-101/Reoplex	✓								✓	103
OV-210	✓								✓	49
OV-210/SE-30	✓								✓	103
OV-225	✓								✓	103
QF-1	✓							✓	✓	143
Reoplex	✓				✓					30
SE-30	✓		✓				✓	✓	✓	17,103,161 (Appendix A)
SE-30/OV-210	✓								✓	103
SP-1000			✓					✓		106
SP-2100	✓		✓					✓	✓	17,106, (Appendix A)
DERIVATIZED PHOSPHORUS COMPOUNDS:										
Carbowax 20M	✓			✓		✓				112
Gas Chrom Q	✓							✓		164
OV-1	✓				✓					112

Table 5B. SULFUR COMPOUNDS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 1500	✓	✓		✓	✓	✓	✓	✓	✓	110
Carbowax 20M		✓	✓		✓	✓	✓	✓	✓	6,14,17,131,136,137,138
DC-200		✓						✓	✓	143
DESG SE		✓							✓	53
FFAP		✓		✓		✓		✓		17,110
OV-1	✓			✓	✓			✓	✓	47,143
OV-17/QF-1		✓			✓					51,87
OV-101	✓	✓		✓	✓	✓		✓		14,31,136,137,138
Porapak Q*	✓								✓	150
QF-1	✓							✓	✓	143
DERIVATIZED SULFUR COMPOUNDS:										
Dexsil 300	✓						✓			94
Gas Chrom Q	✓							✓		164

Table 6B. CARBOHYDRATES

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
OV-101	✓		✓					✓		52

Table 7B. STEROIDS

OATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
V-17	✓							✓		134

Table 8B. ORGANOMETALLIC COMPOUNDS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
DERIVATIZED ORGANOMETALLIC COMPOUNDS:										
OV-17	✓				✓			✓		118

Table 9B. NITROGEN COMPOUNDS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 400	✓				✓	✓		✓		101,110
Carbowax 1500	✓	✓		✓	✓	✓	✓	✓		18,110 (Appendix A)
Carbowax 20M	✓	✓	✓	✓	✓	✓	✓	✓		71,117,131,136,137,138,153,161,173
Chromosorb 101*	✓			✓	✓	✓			✓	36,71,116 (Appendix A)
DC-200	✓			✓	✓			✓		87
Emulphor ON 870			✓		✓			✓		67
FFAP	✓			✓	✓	✓	✓	✓		17,18,71,110
OV-1	✓	✓		✓	✓			✓		24,30,86, (Appendix A)
OV-17	✓				✓	✓	✓	✓		97, (Appendix A)
OV-17/QF-1	✓			✓	✓			✓		87,153
OV-17/QF-210	✓							✓		103
OV-101	✓	✓	✓	✓	✓	✓	✓	✓	✓	31,76,99,117,136,137,138 (Appendix A)
Reoplex	✓							✓		103
OV-210	✓							✓		87
OV-225	✓			✓					✓	103
Porapak Q*	✓								✓	150, (Appendix A)
SE-30	✓		✓	✓	✓	✓	✓	✓		18,103,161, (Appendix A)
SE-30/OV-210	✓								✓	103
SF-96			✓	✓		✓	✓			42, (Appendix A)
SP-1000			✓					✓		106
SP-2100	✓		✓		✓		✓	✓		17,92,106, (Appendix A)
UKW-98	✓				✓	✓	✓			153
DERIVATIZED NITROGEN COMPOUNDS:										
Gas Chrom Q	✓							✓		164

Table 10B. CARBOXYLIC ACIDS AND ANHYDRIDES

OATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Apiezon L	✓	✓		✓						167
ASI Silicone	✓							✓		17
APOLAR-10C Silicone	✓			✓				✓		17
Carbowax 20M	✓		✓		✓			✓		21,47,71,117 (Appendix A)
Carbowax 600-Carbowax 20M	✓			✓						167
Chromosorb 101*				✓	✓					71
Chromosorb 104*	✓			✓						69
Chromosorb * 105 + 750	✓			✓						69
FFAP	✓			✓	✓	✓		✓		17,71,110
OV-1	✓			✓	✓			✓	✓	47,86
OV-17/QF-1	✓				✓			✓		51,87
OV-101	✓				✓					31
OV-210	✓							✓		87
Phosphoric acid	✓			✓	✓					158
Porapak Q*	✓					✓				170
SE-30	✓			✓	✓					39,160
SP-1240 DA	✓			✓	✓	✓	✓	✓		(Appendix A)
Trimer Acid			✓						✓	133
Tween 20	✓			✓						167
DERIVATIZED CARBOXYLIC ACIDS:										
Carbowax 20M	✓	✓		✓	✓	✓	✓	✓		4,91,112
DC-200	✓							✓	✓	143
DEGS		✓				✓				(Appendix A)
Dexsil		✓				✓				(Appendix A)
FFAP	✓			✓						74
OV-1	✓		✓	✓	✓	✓		✓	✓	24,74,112,143

(continued)

Table 10B. (cont'd)

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
OV-17	✓	✓				✓		✓		55,56,57, (Appendix A)
OV-17/QF-1	✓								✓	25
OV-101		✓	✓	✓		✓		✓		74,136,137,138
OV-101/OV-210	✓								✓	25
OV-225	✓								✓	25
QF-1	✓							✓	✓	143
SE-30			✓	✓						74
SF-96			✓	✓						74
SP-1000			✓					✓		106
SP-2100			✓					✓		106
SP-2401										101

Table 11B. PHENOLS AND NAPHTHOLS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 1500	✓				✓	✓		✓		110, (Appendix A)
Carbowax 4000	✓				✓		✓			5
Carbowax 20M	✓	✓	✓		✓	✓	✓	✓	✓	13,21,72,110,117,131,136,137,138,161
DC-200	✓				✓		✓			153
Emulphor ON 870	✓		✓		✓			✓		12,64,67
FFAP	✓				✓			✓		110
OV-1	✓		✓	✓	✓	✓		✓	✓	30,86,112, (Appendix A)
OV-17	✓	✓			✓	✓		✓	✓	29,56,57,96,97,127,162, (Appendix A)
OV-11/QF-1	✓				✓	✓		✓	✓	23,122,153
OV-11/QF-F	✓				✓	✓		✓	✓	125
OV-61	✓		✓		✓	✓		✓		68
OV-101	✓	✓	✓	✓	✓	✓		✓	✓	7,13,31,36.68,72,76,99,117,136, 137,138 (Appendix A)
OV-101/OV-210	✓					✓		✓		23
OV-101/UCON HB			✓			✓		✓		65
OV-225	✓					✓		✓		7,23
SE-30	✓	✓	✓	✓	✓	✓		✓		39,96,110,158,161, (Appendix A)
SE-30/OV-210	✓					✓		✓	✓	122
SE-52			✓						✓	132
SF-96			✓			✓	✓			(Appendix A)
SP-1240 DA	✓			✓	✓	✓	✓	✓		70,123, (Appendix A)
SP-2100	✓				✓					92
Tenax GC*	✓				✓		✓	✓		29,36,123
UCW-98	✓				✓			✓		153
DERIVATIZED PHENOLS AND NAPHTHOLS:										
Carbowax 20M		✓				✓				91
IMOL	✓			✓	✓					124

Table 11B. (cont'd)

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
OV-17	✓							✓		56
SE-30			✓				✓		✓	107
SP-2250/2401	✓							✓		156
SP-2401	✓			✓	✓	✓	✓	✓		101,149
Tenax GC*	✓			✓	✓	✓	✓	✓		149
DEGS		✓				✓	✓			(Appendix A)
Dexsil		✓				✓	✓			(Appendix A)
SP-1000			✓					✓		106
SP-2100			✓					✓		106

Table 12B. AMINES

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 20M	✓	✓	✓	✓	✓	✓		✓	✓	21,57,59,71,131,136,137,138,161
Carbowax 1500	✓				✓	✓				98
Chromosorb 101*	✓			✓	✓					36,71
Chromosorb 103*	✓							✓		57
FFAP	✓				✓	✓			✓	59,71
OV-1	✓			✓	✓			✓		30
OV-17/QF-1		✓			✓					51
OV-101	✓	✓	✓	✓	✓	✓	✓	✓		31,76,136,137,138, (Appendix A)
Pennwalt 223	✓			✓		✓	✓		✓	32,135
Polypropyl -										
amine/SP100	✓							✓		57
SE-30	✓		✓	✓	✓	✓	✓	✓		142,161 (Appendix A)
SE-1000	✓							✓		57
SF-96			✓		✓	✓				(Appendix A)
SP-1000	✓		✓					✓		106,110
SP-2100			✓					✓		106
Tenax GC*	✓				✓					18,36
Carbowax 1500			✓						✓	147
OV-17	✓							✓	✓	75
OV-17/QF-1	✓						✓			80
PEG 20M			✓	✓						78
SF-96		✓		✓						78

Table 13B. NITRO COMPOUNDS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 20M	✓	✓	✓	✓	✓	✓	✓	✓	✓	59,117,131,136,137,151,161 (Appendix A)
Chromosorb 101*	✓				✓					36,136,137,138
FFAP	✓							✓	✓	58,59
OV-1	✓							✓		24
OV-17	✓				✓	✓	✓	✓		97 (Appendix A)
OV-101		✓				✓			✓	136,137, 138
SE-30	✓		✓		✓					142,161 (Appendix A)
SP-1000			✓					✓		106
SP-2100			✓		✓			✓		92,106
Tenax GC*	✓				✓			✓		36

Table 14B. KETONES

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Aue*	✓				✓	✓			✓	90
Carbowax 1500	✓	✓		✓	✓	✓	✓	✓		27,28,38,55,57,100,110,161, (Appendix A)
Carbowax 20M	✓	✓	✓		✓	✓		✓	✓	14,21,47,71,110,117,131,136,137,138 144,161
Chromosorb 101*	✓				✓	✓				36,71
Chromosorb 104*	✓			✓						69
Chromosorb 105 + 750	✓			✓						69
Emulphor ON 870			✓		✓	✓		✓	✓	12,64,67,133,171
FFAP	✓			✓	✓	✓		✓		17,71,110,144
OV-1	✓			✓	✓			✓	✓	30,47,86,121,144
OV-17	✓				✓		✓	✓		56,57,96,97, (Appendix A)
OV-17/QF-1	✓	✓		✓	✓			✓	✓	51,121,145
OV-101	✓	✓	✓	✓	✓	✓	✓	✓		14,31,117,136,137,138
Porapak Q*	✓					✓			✓	150,155
SE-30	✓		✓	✓	✓	✓	✓	✓	✓	79,96,110,161,160,162 (Appendix A)
SE-30/OV-210	✓			✓				✓	✓	121,145
SF-96			✓						✓	133
GE SF-96/ Igepal Co 880			✓					✓	✓	43,44,45
SP-1000			✓					✓		106
SP-2100	✓		✓		✓		✓	✓		92,106 (Appendix A)
Tenax GC*	✓				✓					36
DERIVATIZED KETONES:										
Ethofat	✓			✓						79
OV-17		✓			✓					77
OV-101		✓		✓						77
PEG 20M			✓	✓						77
SF-96		✓					✓			77

Table 15B. ALDEHYDES

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 20M	✓	✓	✓	✓	✓	✓		✓		17,110,117,131,136,137,138,161
Carbowax 1500	✓			✓	✓	✓	✓	✓		28,100,110 (Appendix A)
Chromosorb 101*	✓				✓	✓	✓	✓		10,36
Chromosorb 104*	✓			✓						69
Chromosorb 105 + 750	✓			✓						69
Emulphor ON 870			✓		✓	✓		✓	✓	12,133,171
FFAP	✓				✓		✓	✓		110
OV-1	✓			✓	✓			✓		30,86
OV-17/QF-1		✓		✓						51
OV-101	✓	✓	✓	✓	✓	✓	✓	✓		31,136,137,138,151
OV-101 + UCON HB			✓			✓	✓	✓		65
SE-30	✓		✓	✓	✓	✓	✓	✓	✓	10,81,110,161,158 (Appendix A)
GE SF-96/										
Igepal Co 880										43,44,45
SP-1000			✓					✓		106
SP-2100			✓					✓		106
STAP			✓						✓	133
Tenax GC*	✓				✓					10,36
DERIVATIZED ALDEHYDES:										
Ethofat			✓	✓						79
OV-17		✓		✓						77
OV-101		✓		✓						77
PEG 20M			✓	✓						79
SE-30	✓		✓							79
SF-96			✓	✓						77

Table 16B. ALCOHOLS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 1500	✓			✓	✓	✓	✓	✓		18,27,28,38,100,110 (Appendix A)
Carbowax 20M	✓	✓	✓	✓	✓	✓		✓	✓	17,6,14,47,71,110,117,31,132,136 137,138,144,161
Carbowax 20M + Gas Quat L+ Ionox	✓								✓	82
Chromosorb 101*	✓			✓	✓					18,36,71
Chromosorb 104*	✓			✓						69
Chromosorb 105* + 750	✓			✓						69
DC-200	✓							✓	✓	143
Emulphor ON 870			✓		✓	✓		✓	✓	12,67,132,133,171
FFAP	✓		✓	✓	✓	✓	✓	✓	✓	18,71,110,132,144
OV-1	✓			✓	✓			✓	✓	20,47,86,143,144 (Appendix A)
OV-17	✓	✓			✓		✓			55,57 (Appendix A)
OV-17/QF-1		✓		✓						51
OV-101	✓	✓	✓	✓	✓	✓	✓	✓		31,117,136,137,138,151
OV-101 + Ucon HB			✓			✓	✓	✓		65
Porapak Q*	✓								✓	150
QF-1	✓							✓	✓	143
SE-30	✓		✓	✓	✓	✓	✓	✓	✓	18,81,107,110,161 (Appendix A)
SE-52			✓						✓	132
SF-96			✓	✓		✓	✓		✓	42, 133 (Appendix A)
SF-96 Igepal Co 880			✓	✓				✓	✓	43,44,45
SP-1000	✓		✓					✓		106,116
SP-2100	✓		✓		✓		✓	✓		106 (Appendix A)
Tenax GC*	✓				✓		✓			36,61
1-Trimethyloxy-silyl-2-chloro-methyl phenylethane		✓		✓						14

Table 17B. ESTERS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Aue*	✓				✓	✓			✓	90
Carbowax 1500	✓				✓	✓		✓		37,110 (Appendix A)
Carbowax 4000	✓				✓		✓			5
Carbowax 20M	✓	✓	✓	✓	✓	✓		✓	✓	6,47,71,72,110,117,131,136,137 138,144,161 (Appendix A)
Carbowax 20M + Gas Quat L+	✓									82
Chromosorb 101*	✓				✓					36,71
DEGS	✓		✓			✓	✓			71,111
DC-200	✓							✓	✓	87,143
Emulphor ON 870			✓		✓	✓		✓		12,64
Ethylene Glycol Adipate	✓								✓	84
FFAP	✓			✓	✓	✓		✓		71,110,144
OV-1	✓			✓	✓			✓	✓	15,30,47,86,143,144
OV-17	✓	✓					✓	✓		55,57,66,97 (Appendix A)
OV-17/QF-1	✓							✓	✓	87
OV-61			✓		✓	✓	✓	✓		68
OV-101	✓	✓	✓	✓	✓	✓	✓	✓		5,31,68,117,136,137,138
OV-210	✓							✓	✓	87
OV-225	✓						✓			5,72
QF-1	✓							✓	✓	143
SE-30	✓		✓	✓	✓	✓	✓	✓	✓	39,81,110,114,161 (Appendix A)
SF-96			✓			✓	✓			(Appendix A)
SP-1000			✓					✓		106
SP-2100	✓		✓	✓				✓		92,106
Tenax GC*	✓			✓						36

Table 18B. AMIDES

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 1500	✓			✓				✓		98 (Appendix A)
Carbowax 20M	✓	✓	✓		✓	✓		✓	✓	47,71,111,131,136,137,138,161
Chromosorb 101*	✓				✓	✓				36,71
DC-200	✓							✓	✓	143
FFAP	✓				✓	✓				71
OV-1	✓			✓	✓		✓	✓		30,47,143
OV-101	✓	✓	✓	✓	✓	✓	✓	✓		31,117,136,137,138
OV-17	✓					✓	✓	✓		56 (Appendix A)
QF-1	✓							✓	✓	143
SP-1000			✓					✓		106
SP-2100			✓					✓		106
Tenax GC*	✓				✓					36
DERIVATIZED AMIDES:										
Dexsil 300	✓						✓			94

Table 19B. ETHERS AND HETEROCYCLIC OXYGEN COMPOUNDS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 1500	✓			✓	✓	✓	✓	✓		28,83,100,110 (Appendix A)
Carbowax 20M	✓	✓	✓	✓	✓	✓		✓	✓	17,47,110,117,131,136,137,138
Chromosorb 101*	✓				✓					36
DC-200	✓							✓	✓	143
Emulphor ON 870			✓		✓	✓		✓		12,64,67
FFAP	✓				✓	✓		✓		110
OV-1	✓			✓	✓			✓	✓	30,47,86,143
OV-17	✓				✓		✓	✓		56,96,97 (Appendix A)
OV-101	✓	✓	✓	✓	✓	✓	✓	✓		31,117,136,137,138
OV-225	✓								✓	53 (Appendix A)
QF-1	✓							✓	✓	143
SE-30	✓		✓		✓	✓	✓	✓		189,39,96,110,157 (Appendix A)
SE-52			✓						✓	133
GE SF-96 Igepal Co 880			✓					✓	✓	43,44,45
SF-96			✓			✓	✓			(Appendix A)
SP-1000			✓					✓		106
SP-2100			✓		✓			✓		92,106
Tenax GC*	✓				✓					36

Table 20B. POLYNUCLEAR AROMATIC HYDROCARBONS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 20M	✓	✓	✓		✓	✓	✓	✓		13,118,131,136,137,138,144
DEGS	✓						✓			111
Dexsil 300	✓								✓	85
Dexsil 400	✓				✓				✓	33,146
Emulphor ON 870			✓		✓	✓		✓		12
Igepal Co 800		✓					✓	✓		(Appendix A)
OV-1	✓									30,86,144
OV-7	✓	✓	✓		✓	✓	✓	✓		1 (Appendix A)
OV-17	✓				✓		✓	✓		56,96,97,127,162 (Appendix A)
OV-17/QF-1	✓	✓			✓			✓	✓	51,87
OV-17/QF-F	✓				✓					125
OV-17/OV-210	✓			✓	✓	✓	✓	✓		104
OV-61			✓		✓	✓	✓	✓		68
OV-101	✓	✓	✓	✓	✓	✓	✓	✓	✓	7,13,31,36,68,99,117,136,137,138 (Appendix A)
OV-101 UCON HB	✓					✓	✓	✓		65
OV-210	✓					✓		✓	✓	87,162
RbCl	✓								✓	85
SE-30	✓	✓	✓		✓		✓	✓	✓	96,115,161,158,160 (Appendix A)
SE-30/OV-210	✓			✓	✓	✓	✓	✓		104
SE-52			✓			✓	✓	✓		(Appendix A)
SP-1000			✓					✓		106 (Appendix A)
SP-2100			✓	✓	✓			✓		92,106 (Appendix A)

Table 21B. BENZENOID HYDROCARBONS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 20M	✓	✓	✓		✓	✓	✓	✓	✓	14,47,110,117,131,136,137,138,144,161
Carbowax 1500	✓		✓	✓	✓	✓	✓	✓		19,28,55,57,100,110,117 (Appendix A)
Carbowax 1000	✓					✓	✓			5
Chromosorb 101*	✓				✓	✓	✓	✓		10,36,129
Emulphor ON 870	✓		✓		✓	✓		✓		12
FFAP	✓			✓	✓	✓	✓	✓		19,144
OV-1	✓			✓	✓			✓	✓	17,30,40,41,47,86,144
OV-17	✓	✓			✓	✓	✓	✓		56,96,97,110 (Appendix A)
OV-17/QF-1		✓		✓					✓	51,113
OV-61			✓		✓	✓	✓	✓		67
OV-101	✓	✓	✓	✓	✓	✓	✓	✓	✓	5,17,14,31,68,113,117,137,138,151
OV-101 + UCON - HB			✓			✓	✓	✓		65
OV-225	✓						✓			5
SE-30	✓		✓	✓	✓	✓	✓	✓		10,17,39,40,41,96,110,161 (Appendix A)
SE-52			✓					✓		(Appendix A)
GE SF-96	✓		✓		✓	✓	✓	✓	✓	42,69,111 (Appendix A)
GE SF-96/Igepal Co 880			✓					✓	✓	43,44,45
SP-1000	✓		✓					✓		106,110
SP-2100	✓		✓	✓				✓		17,92,106
Tenax GC*	✓			✓	✓	✓	✓	✓		19,36,154
UCON HB 5100			✓		✓			✓		67
UCON LB550			✓		✓			✓		67
UCW-98	✓					✓				88

Table 22B. ALKENES, ALKYNE, AND TERPENOID HYDROCARBONS

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Carbowax 1500	✓			✓	✓	✓	✓	✓		8,28,110 (Appendix A)
Carbowax 20M	✓		✓		✓	✓	✓	✓		14,71,110,117,131,142,161
Chromosorb 101*	✓				✓	✓				71
Emulphor ON 870			✓		✓			✓		64,67
FFAP	✓				✓	✓		✓		71,110
Igepal Co 880		✓					✓	✓		(Appendix A)
OV-1	✓			✓	✓			✓		30,86
OV-17	✓						✓	✓		57,97 (Appendix A)
OV-61			✓		✓	✓	✓	✓		68
OV-101	✓		✓	✓	✓	✓	✓	✓		14,31,68,117
OV-101 + UCON HB			✓			✓	✓	✓		65
SE-30			✓	✓			✓		✓	81, 161 (Appendix A)
GE SF-96			✓	✓		✓	✓			42 (Appendix A)
GE SF-96 Igepal Co 880			✓					✓	✓	43,44,45
SP-1000			✓					✓		106
UCON HB 5100			✓		✓	✓	✓	✓		67

Table 23B. ALKANES

COATING	COLUMN TYPE			WATER MATRIX						REFERENCES
	Packed	SCOT	WCOT	Distilled	Drinking	Industrial	Municipal	Surface	Other	
Aue*	✓				✓	✓				90
Carbowax 1500	✓			✓	✓	✓	✓	✓		27,28,55,110,133 (Appendix A)
Carbowax 20M	✓		✓	✓			✓		✓	13,71,83,117,131,144,161
Chromosorb 101*	✓				✓	✓	✓	✓		10,36,71,110
Emulphor ON 870	✓		✓		✓	✓		✓		12,67,64
FFAP	✓			✓	✓	✓	✓	✓		71,110,144
Igepal Co 880		✓					✓	✓		(Appendix A)
OV-1	✓		✓	✓	✓			✓		15,30,45,41,86,144
OV-17	✓			✓	✓	✓	✓	✓		96,96,119 (Appendix A)
OV-61			✓		✓	✓	✓	✓		68
OV-101	✓	✓	✓	✓	✓	✓	✓	✓	✓	14,13,31,68,117,151
OV-101 + UCON HB			✓			✓	✓	✓		65
SE-30	✓	✓	✓	✓	✓	✓	✓	✓	✓	10,17,40,41,81,96,110,161,158 (Appendix A)
GE SF-96			✓	✓		✓	✓			42 (Appendix A)
GE SF-96 Igepal Co 880			✓	✓				✓	✓	43,44,45
SP-1000	✓		✓					✓		106,110
SP-2100	✓		✓		✓			✓		92,106,141
Tenax GC*	✓				✓					36
UCON-HB 5100			✓		✓			✓		67

REFERENCES

1. Acheson, M. A., R. M. Harrison, R. Perry, R. A. Wellings, Water Res., 10, 207 (1976).

2. Agemian, H., A. S. Chau, J. Assoc. Offic. Anal. Chem., 60, 1070 (1977).

3. Alhoff, M., B. Josefsson, Anal. Chem., 46, 658 (1974).

4. Aue, W. A., C. R. Hastings, K. O. Gerhardt, J. O. Pierce, II., H. H. Hill, R. F. Moseman, J. Chromatog., 72, 259 (1972).

5. Austern, B. M., J. M. Cohen, R. A. Dobbs, Environ. Sci. Technol., 2, 588 (1975).

6. Bassette, R., S. Ozeris, C. H. Whitnah, Anal. Chem., 34, 1540 (1962).

7. Bean, R. M., R. G. Riley, P. W. Ryan, Investigation of Halogenated Components Formed from Chlorination of Marine Water, in Water Chlorination: Environmental Impact and Health Effects, Vol. 1, R. L. Jolley, ed., Ann Arbor Science, Ann Arbor, Michigan (1978), 223 pp.

8. Beggs, D. P., Amer. Lab., July (1978) 81 pp.

9. Beggs, D. P., GC/MS Analysis of Volatile Organics in Water, Hewlett-Packard Application Note, AN176-24.

10. Bellar, T. A., J. T. Lichtenberg, The Determination of Volatile Organic Compounds at the μg/ℓ Level in Water by Gas Chromatography, National Environmental Research Center, Cincinnati, Ohio, November, (1974), NTIS PB-237 973/3ST, 69 pp.

11. Bellar, T. A., J. J. Lichtenberg, J. W. Eichelberger, Environ. Sci. Technol., 10, 926 (1976).

12. Bertsch, W., E. Anderson, G. Holzer, J. Chromatogr., 112, 701 (1975).

13. Bertsch, W., E. Anderson, G. Holzer, J. Chromatogr., 126, 213 (1976).

14. Bertsch, W., E. Anderson, G. Holzer, J. Chromatogr., (1977).

15. Boehm, P. D., J. G. Quinn, Geo. Cosmo. Acta, 37, 2459 (1973).

16. Bromilow, R. H., K. A. Lord, J. Chromatogr., 125, 495 (1976).

17. Budde, W. L., Solubility Separation by pH Adjustment: A Procedure for the Extraction of Industrial Organic Chemicals in Effluents and Streams, U. S. Environmental Protection Agency, Athens, GA, WO-1/75.

18. Budde, W. L., Distillation: A Procedure for Watersoluble Volatile Organic Solvents in Effluents and Streams, U. S. Environmental Protection Agency, Cincinnati, Ohio, W33-12/74.

19. Budde, W. L., Headspace Analysis: A Quick Qualitative Technique for Volatile Organic Compounds, U. S. Environmental Protection Agency, Athens, Georgia, HV01-75.

20. Budde, W. L., J. H. Eichelberger, J. Chromatogr., 134, 147 (1977).

21. Burnham, A. K., G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec, R. Willis, Anal. Chem., 44, 139 (1972).

22. Burchfield, H. P., E. E. Storrs, J. Chromatogr. Sci., 13, 202 (1975).

23. Chau, A. S., J. A. Coburn, J. Assoc. Offic. Anal. Chem., 57, 389 (1974).

24. Chau, Y. K., M. E. Fox, J. Chromatogr. Sci., 9, 271 (1971).

25. Chau, A. S., K. Terry, J. Assoc. Offic. Anal. Chem., 58, 1296 (1975).

26. Chian, E. S. K., W. N. Bruce, H. H. P. Fang, Environ. Sci. Technol., 9, 52 (1975).

27. Chian, E. S. K., P. P. K. Kuo, W. S. Cooper, W. F. Cowen, R. C. Fuentes, Environ. Sci. Technol., 11, 282 (1977).

28. Chian, E. S. K., H. Meng, F. B. DeWalle, Protocols for Measuring Purgeable Organics in Sewage and Sludge, Item B (1977) 27 pp.

29. Chriswell, C. C., R. C. Chang, J. S. Fritz, Anal. Chem., 47, 1325 (1975).

30. Chriswell, C. D., R. L. Ericson, G. A. Junk, K. W. Lee, J. S. Fritz, H. J. Svec, J. Amer. Water Works Assoc., 669 (1977) (Dec.).

31. Chriswell, C. D., R. L. Ericson, G. A. Junk, K. W. Lee, J. S. Fritz, H. J. Svec, Comparison of Macroreticular Resins and Activated Carbon as Sorbents for Accumulating Organic Compounds from Drinking Water, Ames Laboratory, Iowa State University, Ames, Iowa, 25 pp.

32. Chriswell, C. D., J. S. Fritz, J. Chromatogr., 136, 9891 (1977).

33. Clark, B. R., M. R. Guerin, Chemical Characterization and Monitoring Studies of Effluents from Emerging Fossil Fuel Processes, Oak Ridge National Laboratory, Oak Ridge, Tennessee, NTIS CONF 761131-1, 9 pp.

34. Coburn, J. A., L. A. Valdmanis, A. S. Y. Chau, J. Assoc. Offic. Anal. Chem., 60, 224 (1977).

35. Personel Communication, Appendix A.

36. Coleman, W. E., R. D. Lingg, R. G. Melton, F. C. Kopfler, The Occurrence of Volatile Organics in Five Drinking Water Supplies Using Gas Chromatography/Mass Spectrometry, in Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Michigan (1976), 305 pp.

37. Personal Communication, Appendix A.

38. Cowen, W. F., W. J. Cooper, J. W. Highfill, Anal. Chem., 47, 2483 (1975).

39. Deinzer, M., R. Melton, D. Mitchell, Water Research, 9, 799 (1975).

40. Dell'Acqua, R., B. Bush, J. Egan, J. Chromatogr., 128, 271 (1976).

41. Dell'Acqua, R., J. A. Egan, B. Bush, Environ. Sci. Technol., 9, 38 (1975).

42. Dowty, B. J., S. R. Antoine, J. L. Laseter, Quantitative and Qualitative Analysis of Purgeable Organics by High Resolution Gas Chromatography and Flame Ionization Detection, University of New Orleans, 21 pp.

43. Dowty, B. J., D. R. Carlisle, J. L. Laseter, Science, 187, 75 (1975).

44. Dowty, B. J., D. R. Carlisle, J. L. Laseter, Environ. Sci. Technol., 9, 762 (1975).

45. Dowty, B., J. L. Laseter, Anal. Letters, 8, 25 (1975).

46. Dunker, J. C., M. Hillebrand, J. Chromatogr., 150, 195 (1978).

47. Dunlap, W. J., D. C. Shew, M. R. Scalf, R. L. Cosby, J. M. Robertson, Isolation and Identification of Organic Contaminants in Ground Water in Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, Ann Arbor, Michigan (1976), 453 pp.

48. Eichelberger, J. W., L. E. Harris, W. L. Budde, Anal. Chem., 46, 227 (1974).

49. Eichelberger, J. W., L. E. Harris, W. L. Budde, Anal. Chem., 47, 495 (1975).

50. Eichelberger, J. W., J. J. Lichtenberg, J. Amer. Water Works Assoc., 63, 25 (1971).

51. Eichelberger, J. W., W. M. Middleton, W. L. Budde, Analytical Quality Assurance for Trace Organics Analysis by Gas Chromatography/ Mass Spectrometry, U. S. Department of Commerce, NTIS PB245 823, September (1975) 12 pp.

52. Ekeund, G., B. Josefsson, C. Roos, J. Chromatogr., 142, 575 (1977).

53. Ellgenhausen, D., Anal. Letters, 8, 11 (1975).

54. Energy Resources, Accumulation of Organic Pollutants by Solid Adsorbents, U. S. Environmental Protection Agency, Washington, DC, October, 1975, #68-01-2925.

55. Ewing, B. B., E. S. K. Chian, J. C. Cook, C. A. Evan, P. K. Hopke, E. G. Perkins, Monitoring to Detect Previously Unrecognized Pollutants, University of Illinois, U. S. Environmental Protection Agency, Progress Report No. 1, November 1975, EPA Contract No. 68-01-3234.

56. Ewing, B. B., E. S. K. Chain, J. C. Cook, C. A. Evans, P. K. Hopke, E. G. Perkins, Monitoring to Detect Previously Unrecognized Pollutants, University of Illinois, U. S. Environmental Protection Agency, Progress Report No. 2, February 1976, EPA Contract No. 68-01-3234.

57. Ewing, B. B., E. S. K. Chian, J. C. Cook, C. A. Evans, P. K. Hopke, E. G. Perkins, Monitoring to Detect Previously Unrecognized Pollutants, University of Illinois, U. S. Environmental Protection Agency, Progress Report No. 4, August, 1976, EPA Contract No. 68-01-3234, 215 pp.

58. Fine, D. H., D. P. Rounbehler, N-Nitroso Compounds in Water in Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed. Ann Arbor Science, Ann Arbor, MI (1976) 255 pp.

59. Fine, D. H., D. P. Rounbehler, N. P. Sen, J. Agri. Food Chem., 24, 980 (1976).

60. Ford, J. H., C. A. McDaniel, F. C. White, R. E. Vest, R. E. Roberts, J. Chromatogr. Sci., 13, 291 (1975).

61. Fox, M. E., Environ. Sci. Technol., 7, 838 (1973).

62. Fujii, T., Anal. Chem., 49, 1985 (1977).

63. Fujii, T., J. Chromatogr., 139, 297 (1977).

64. Gehrike, C. W., H. Nakamoto, R. W. Zumwalt, J. Chromatogr., 45, 24 (1969).

65. Giger, W., M. Reinhard, C. Schauffner, F. Zurcher, Analysis of Organic Constituents in Water by High Resolution Gas Chromatography in Combination with Specific Detection and Computer-Assisted Mass Spectrometry, in Identification and Analysis of Organic Pollutatns in Water, L. H. Keith, ed., Ann Arbor Science, Ann Arbor, MI, (1976) 433 pp.

66. Gough, K. M., H. D. Gesser, J. Chromatogr., 115, 383 (1975).

67. Grob, K. G. Grob, J. Chromatogr., 90, 303 (1974).

68. Grob, K., K. Grob, Jr., G. Grob, J. Chromatogr., 106, 299 (1976).

69. Grob, R. L., M. A. Kaiser, J. Environ. Sci. Health, All, 623 (1976).

70. Hall, J. R., M. N. Wass, Problems Encountered with EPA Protocol Procedure for Screening of Industrial Waste Effluents for Priority Pollutatns, American Chemical Society, Environmental Division, Miami, September, 1978.

71. Harris, L. E., W. L. Budde, J. W. Eichelberger, Anal. Chem., 46, 1912 (1974).

72. Hartigan, M. J., K. Billeb, L. S. Ettre, Chromatographia, 10, 571 (1977).

73. Harvey, G., Adsorption of Chlorinated Hydrocarbons from Seawater by a Cross-linking Polymer, U. S. Environmental Protection Agency, National Marine Water Quality Laboratory CQ, 16020., November, 1972.

74. Hattlela, M. L., T. Raisanen, Bull. Environ. Contam. Toxicol., 16, 355 (1976).

75. Hermann, V., T. Juttner, Anal. Biochem., 78, 365 (1977).

76. Holder, C. L., J. R. King, J. Toxi. Environ. Health, 2, 111 (1976).

77. Hoshika, Y., J. Chromatogr., 120, 379 (1976).

78. Hoshika, Y., J. Chromatogr., 136, 253 (1977).

79. Hoshika, Y., J. Chromatogr., 152, 224 (1978).

80. Howland, R. G., C. J. Wallace, Chlorine and Activated Carbon Treatment for Removal of Toxic Substances from Water in Water Chlorination: Environmental Impact and Health Effects, Vol. 1, R. L. Jolley, ed., Ann Arbor Science, Ann Arbor, MI, (1978) 659 pp.

81. Jennings, W. G., M. Filsoof, J. Agri. Food Chem., 25, 440 (1977).

82. Jennings, W. G., R. Wohleb, M. J. Lewis, J. Food Sci., 37, 69 (1972).

83. Jeone, J. T., G. A. Reineccius, E. D. Thomas, J. Agri. Food Chem., 24, 433 (1976).

84. Joe, F. J. Jr., D. A. Keine, J. Assoc. Offic. Anal. Chem., 60, 509 (1977).

85. John, E. D., G. Nickless, J. Chromatogr., 138, 399 (1977).

86. Junk, J. A., J. J. Richard, M. D. Grieser, J. Chromatogr., 99, 745 (1974).

87. Junk, G. A., J. T. Richard, H. J. Svec, J. S. Fritz, J. Amer. Water Works Assoc., 68, 218 (1976).

88. Jurinski, N. B., G. E. Podolak, T. L. Hess, Am. Ind. Hyg. Ass. J., 36, 497 (1975).

89. Kaiser, K. L. E., B. G. Oliver, Anal. Chem., 48, 2207 (1976).

90. Karasek, F. W., Ind. Res. Develop., April (1978), 113 pp.

91. Keith, L. H., Environ. Sci., Technol., 10, 555 (1976).

92. Keith, L. H., A. W. Garrison, T. F. Allen, M. H. Carter, T. L. Floyd, J. D. Pope, A. D. Thurston, Jr., Identification of Organic Compounds in Drinking Water from Thirteen U. S. Cities in Identification and Analysis of Organic Pollutants in Water, L. H. Keith, ed., Ann Arbor Science, Ann Arbor, MI (1976), 329 pp.

93. Khan, S. U., K. S. Lee, J. Agri. Food Chem., 24, 684 (1976).

94. King, J. R., M. C. Bowman, Biochem. Medicine, 12, 313 (1975).

95. Kirsten, W. J., P. E. Mattsson, Anal. Chem., 47, 1974 (1975).

96. Kleopfer, R. D., Analysis of Drinking Water for Organic Compounds in Identification and Analysis of Organic Pollutants in Water, L H. Keith, ed., Ann Arbor Science, Ann Arbor, MI (1976), 399 pp.

97. Kleopfer, R. D., Bunn, W. W., Cleanup of Sewage Sludge Extracts by Gel Permeation Chromatography, U. S. Environmental Protection Agency, Kansas City, KA, August 1978.

98. Kubelka, V., J. Mitera, V. Rabl, J. Mostecky, Water Res., 10, 137 (1976).

99. Kuehl, D. W., G. D. Veith, E. N. Leonard, Brominated Compounds Found in Waste Treatment Effluents and Their Capacity to Bioaccumulate, in Water Chlorination: Environmental Impact and Health Effects, Vol. 1, R. L. Jolley, ed., Ann Arbor, Science, Ann Arbor, MI (1978), 175 pp.

100. Kuo, P. P. K., E. S. K. Chian, P. B. DeWalle, Anal. Chem., 49, 1023 (1977).

101. Larson, R. A., A. L. Rockwell, J. Chromatogr., 139, 186 (1977).

102. Larson, R. A., J. C. Weston, J. M. Howell, J. Chromatogr., 111, 43 (1975).

103. Leicht, R., M. Schofield, L. D. Johnson, R. Waltz, Methylene Chloride/Cyclohexane Solvent System Applied to Automated Gel Permeation Cleanup of Residue Samples for Organophosphate, Triazine and Carbamate Pesticides, Analytical Biochemistry Laboratories, Inc., Columbia, MO, 48 pp.

104. Lewis, R. G., Accuracy and Trace Organic Analysis, U. S. Department of Commerce, (1976), NTIS PB-278-375, 34 pp.

105. Lichtenberg, J. T., Methods for the Determination of Specific Organic Pollutatns in Water and Wastewater, IEEE Transactions on Nuclear Sci., NS-22, 874 (1975).

106. Lin, D. C. K., D. A. Contos, R. L. Foltz, V. R. Goff, T. L. Hayes, P. P. Kelly, S. V. Lucas, B. S. Mackay, B. A. Petersen, L. E. Silvon, R. Warren, S. C. Watson, GC/MS Analysis of Organics in Drinking Water Concentrates and Advanced Waste Treatment Concentrates; U. S. Environmental Protection Agency, Cincinnati, OH, November, 1978, Project No. 68-03-2548.

107. Lindstrom, K., J. Nordin, J. Chromatogr., 128, 13 (1976).

108. Lingg, R. D., R. G. Melton, F. C. Kopfler, W. E. Coleman, D. W. Mitchell, J.A.W.W.A., 69, 605 (1977).

109. Little, A. D., Development of Protocols for Analysis of Priority Pollutant Pesticides and PCB in Raw Municipal Wastewater, U. S. Environmental Protection Agency, Cincinnati, OH (1978) 52 pp.

110. Loy, E. W., Jr., J. A. Little, D. W. Brown, J. H. M. Stephensen, Uses of Wastewater Discharge Compliance Monitoring Data, U. S. Environmental Protection Agency, Athens, GA, 25 pp.

111. Manka, J., M. Rebhun, A. Mandelbaum, A. Bortinger, Environ. Sci. Technol., 8, 1017 (1974).

112. Marcus, M., J. Spigarelli, H. Miller, Organic Compounds in Organophosphorus Pesticide Manufacturing Wastewaters, Midwest Research Institute, U. S. Environmental Protection Agency, Contract #68-03-2343.

113. Mattsson, P. E., A. Norstrom, C. Rappe, J. Chromatogr., 111, 209 (1975).

114. Matsuda, K., M. Schnitzer, Bull. Environ. Toxicol., 6 (1971).

115. May, W. C., S. N. Chester, S. P. Chan, B. H. Grump, H. S. Hertz, D. P. Engonion, S. M. Depzel, J. Chromatogr. Sci., 13, 535 (1975).

116. McNeal, T., W. C. Brumley, C. Breder, J. Assoc. Offic. Anal. Chem., Jan. (1979).

Jan. (1979).

117. Meiggs, T. O., Organic Identification by Glass Capillary Gas Chromatograph, U. S. Environmental Protection Agency, Denver, CO, August (1978), 51 pp.

118. Meinema, H., Environ. Sci. Technol., 12, 288 (1978).

119. Mieure, J. P., J. Am. Waer Works Assoc., 69, 62 (1977).

120. Miles, J. W., W. E. Dale, F. C. Churchill, Arch. Environ. Contam., 5, 29 (1976).

121. Moseman, R. F., H. L.Crist, R. T. Edgerton, M. K. Ward, Arch. Environ. Contam. Toxicol., 6, 221 (1977).

122. Moseman, R. F., H. L. Crist, T. R. Edgerson, M. K. Ward, Electron Capture Gas Chromatographic Determination of Kepone Residues in Environmental Samples, U. S. Department of Commerce, November, 1976, NTIS PB-278-594.

123. Mousa, J. J., Symposium on Measurement of Organic Pollutants in Water and Wastewaters, ASTM Committee 0-19, Denver, CO, June (1978).

124. Murray, D. A. J., J. Fish Res. Borad Cana., 32 (2) (1975).

125. Musty, P. R., G. Nickless, J. Chromatogr., 89, 185 (1974).

126. Musty, P. R., G. Nickless, J. Chromatogr., 100, 83 (1974).

127. Musty, P. R., G. Nickless, J. Chromatogr., 120, 369 (1976).

128. Nicholson, A. A., O. Meresz, Bull. Environ. Cont. Toxicol., 14, 453 (19).

129. Nicholson, A. A., O. Meresz, Organics in Ontario Drinking Waters, Part I., The Occurence and Determination of Free and Total Potential Haloforms, Ontario Ministry of the Environment, March, 1976.

130. Nicholson, A. A., O. Meresz, K. Lemyk, Anal. Chem., 49, 814 (1977).

131. Novak, J., J. Zlutecky, V. Kubelka, J. Mostecky, J. Chromatogr., 76, 45 (1973).

132. Novotny, M., M. K. Lee, K. D. Bartle, Chromatographia, 7, 333 (1974).

133. Novotny, M., M. L. McConnell, M. L. Lee, R. Farlow, Clin. Chem., 20, 9 (1974).

134. Okuno, J., Bull. Environ. Cont. Toxicol., 18, 428 (1977).

135. Onuska, F. J., Water Research, 7, 835 (1973).

136. Pellizzari, E. D., N. P. Castillo, Organic Constituents of Water Associated with Coal and Oil Shale Conversion, Glattenburg Conference, 1978.

137. Pellizzari, E. D., N. P.Castillo, S. Willis, D. Smith, J. Bursey, Identification of Organic Constituents in Aqueous Effluenets from Energy-related Processes. Fuel Chemistry, in press.

138. Pellizzari, E. D., N. P. Castillo, S. Willis, D. Smith, J. Bursey, ASTM, in press.

139. Pfaender, F. K., R. B. Jones, A. A. Stevens, Environ. Sci. Technol., 12, 438 (1978).

140. Ramstad, T., N. H. Mable, R. Matalon, Anal. Chem., 49, 386 (1977).

141. Rappaport, L. M., D. A. Fraser, Anal. Chem., 48, 476 (1976).

142. Ray, S., J. Chromatogr., 153, 173 (1978).

143. Robertson, J. M., C. R. Toussaint, M.A. Jorque, Organic Compounds Entering Ground Water from a Landfill, U. S. Environmental Protection Agency, Washington, D. C., September, 1974, EPA-660/2-74-007.

144. Ryan, J. P., J. S. Fritz, J. Chromatogr. Sci., 16, 488 (1978).

145. Saleh, F. Y., G. F. Lee, Environ. Sci. Technol., 12, 297 (1978).

146. Saxena, J., D. Baser, J. Rozuchauski, Method Development and Monitoring of PAH's in Selected U. S. Waters, U. S. Environmental Protection Agency, July 1977, EPA-R-80-3977.

147. Sen, N. P., W. F. Miles, S. Seaman, J. F. Lawrence, J. Chromatogr., 128, 169 (1976).

148. Shadoff, L. A., R. A. Hummel, L. Lamparski, Bull. Environ. Contam. Toxicol., 18, 478 (1977).

149. Shackelford, W. M. , R. G. Webb, Survey Analysis of Phenolic Compounds in Industrial Effluents by GC/MS, U. S. Environmental Protection Agency, Athens, Georgia, 24 pp.

150. Sickels, T. W., D. T. Stafford, Amer. Lab., May (1977), 17 pp.

151. Sievers, R. E., R. H. Shapiro, H. F. Walton, G. A. Eiceman, R. M. Barkley, High Resolution Gas Chromatographic Determination of Organic Compounds in Ozonized Wastewater in High Resolution Gas Chromatography, S. P. Cram, Ed., Academic Press, New York, 1978.

152. Siezen, R. J., T. H. Mague, J. Chromatogr., 130, 151 (1977).

153. Smillie, R. D., A. A. Nicholson, O. Meresz, W. K. Duholke, G. A. V. Rees, K. Roberts, C. Fung, Organics in Ontario Drinking Waters, Part II, Ontario Ministry of the Environment, 07C7703, April, 1977. Project No. AAN-7504.

154. Smillie, R. D., T. Sakuma, W. K. Duholke, J. Environ. Sci. Health, A13, 187 (1978).

155. Smith, J. S., D. F. Durkett, J. M. Hanraker, Determination of Hexachloroacetone and Hexafluoroacetone in Industrial Wastewaters, Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey.

156. Stallings, D. L., L. M. Smith, J. D. Petty, Approaches to Comprehensive Analyses of Persistent Halogenated Environmental Contaminants, Symposium on Measurement of Organic Pollutants in Water and Wastewater, June, 1978. Denver, Colorado.

157. Stancher, B., F. Tunis, L. Favretto, J. Chromatogr., 131, 309 (1977).

158. Stepan, L. F., J. F. Smith, Water Research, 11, 339 (1977).

159. Stolzberg, R. J., D. N. Hume, Anal. Chem., 49, 37 (1974).

160. Suffet, I. H., L. Brenner, J. T. Coyle, P. R. Cairo, Environ. Sci. Technol., 12, 1315 (1978).

161. Suffet, I. H., L. Brenner, J. V. Radziul, GC/MS Identification of Trace Organic Compounds in Philadelphia Waters, in Identification and Analysis of Organic Pollutants in Water, Lawrence H. Keith, Ed., Ann Arbor Science, Ann Arbor, Michigan (1976), 375 pp.

162. Suffet, I. H., L. Brenner, B. Silvex, Environ. Sci. Technol., 10, 1273 (1976).

163. Sutton, C., J. A. Calder, Environ. Sci. Technol., 8, 654 (1974).

164. Thompson, J. F., S. J. Reid, E. J. Kantor, Arch. Environ. Contam. Toxicol., 6, 143 (1977).

165. Tincher, W. C., Chlorination Practices in the Textile Industry, in Water Chlorination: Environmental Impact and Health Effects, Vol. 1, R. L. Jolley, Ed., Ann Arbor Science, Ann Arbor, Michigan (1978), 775 pp.

166. Trussel, A. R., M. D. Umphres, L. Y. C. Leong, R. R. Trussell, Optimizing Trihelomethane Analyses in Water Chlorination: Environmental Impact and Health Effects, Vol. 1, R. L. Jolley, Ed., Ann Arbor Science, Ann Arbor, Michigan (1978), 543 pp.

167. Vitenberg, A. G., V. N. Borisov, V. A. Isidorova, J. Chromatogr., 104, 51 (1975).

168. Vogt, C. R., K. R. Leimer, Trace Sub. Environ. Health, 11, 358 (1977).

169. Wells, D. E., S. J. Johnstone, J. Chromatogr., 140, 17 (1977).

170. White, W. R., J. A. Leenheer, J. Chromatogr. Sci., 13, 386 (1975).

171. Zlatkis, A., W. Bertsch, D. A. Bafus, H. M. Liebick, J. Chromatogr., 91, 379 (1974).